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ELECTRICAL CONDUCTIVITY, VISCOSITY AND DENSITY OF SYSTEMS $SnCl_4 - n\text{-}C_4H_9 - C_6H_6$ AND $SnCl_4 - n\text{-}C_5H_{11}OH - C_6H_6$. II.

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The results of a physicochemical analysis of the systems formed by stannic chloride with n-butyl and n-amyl alcohols are described in this communication.

Stannic chloride, benzene and the alcohols were purified as described earlier [1]. The n-butyl alcohol had the constants: b.p. 113.5°/693.4 mm, d^{20}_4 0.8092, $n^{20}D$ 1.3990; literature data: b.p. 117.0/760 mm, d^{20}_4 0.8099 (0.8094), $n^{20}D$ 1.39909; n-amyl alcohol: b.p. 135.3/702.5 mm, d^{20}_4 0.8139, $n^{20}D$ 1.4101; literature data: b.p. 137.8°/760 mm, d^{20}_4 0.8144, $n^{20}D$ 1.4101 (1.4104).

The method of making the measurements was described in the previous paper [1].

1. The system $SnCl_4 - n\text{-}C_4H_9OH$ was studied as to the viscosity, density and electrical conductivity at 20, 40 and 60°, and also when diluted with 70 mole % of benzene. The results of the measurements are given in Table 1 and plotted in Fig. 1. An examination of Fig. 1 reveals that the viscosity isotherms pass through a maximum at approximately 30 mole % stannic chloride. Increasing the temperature causes the maximum of the viscosity to shift slightly toward the alcohol. When the temperature is lowered the maximum strives toward the ordinate, corresponding to the compound $SnCl_4 \cdot 2C_4H_9OH$. That a compound of such composition is formed is also indicated by the shape of the curve, expressing the dependence of the constant B of the equation $\eta = Ae^{\frac{B}{RT}}$ on the composition. This curve passes through a maximum at 33 mole % stannic chloride.

Solutions of stannic chloride and n-butyl alcohol in benzene have an electrical conductivity of the order of $10^{-4}ohm^{-1}cm^{-1}$, whereas the starting components are nonconducting. The isotherms of the specific electrical conductivity pass through a maximum at 27-28 mole % stannic chloride. The maximum of the corrected electrical conductivity is found at approximately 29 mole % stannic chloride, which, in our opinion, indicates that the two compounds, $SnCl_4 \cdot 2C_4H_9OH$ and $SnCl_4 \cdot 3C_4H_9OH$, are present in the liquid phase at the same time.

2. The system $SnCl_4 - n\text{-}C_5H_{11}OH$ was also studied as to the electrical conductivity, viscosity and density at 20, 40 and 60°, and also when diluted with 70 mole % of benzene. The results of measuring the properties are given in Table 2; the plots of the property–composition diagrams are shown in Fig. 2.

The viscosity of the solutions, beginning from the stannic chloride side, increases, passes through a maximum value at 30-31 mole % stannic chloride and then drops down to the alcohol. When the temperature is lowered the maximum strives toward the ordinate of the compound $SnCl_4 \cdot 2C_5H_{11}OH$, which indicates that a compound of composition 1 : 2 is formed in the system. The curve for the dependence of B on the composition passes through a maximum at 33 mole % stannic chloride, which also indicates the formation of compound $SnCl_4 \cdot 2C_5H_{11}OH$.

The isotherms of the specific electrical conductivity pass through a maximum in the concentration range of 28-30 mole % stannic chloride. Correction for the viscosity does not change the quantitative shape of the electrical conductivity isotherms. The isotherms of the corrected electrical conductivity pass through a maximum at 29-30 mole % stannic chloride, which, in our opinion, indicates the existence of the two compounds, $SnCl_4 \cdot 2C_5H_{11}OH$ and $SnCl_4 \cdot 3C_5H_{11}OH$, in the solution.

TABLE 1.

Mole %, $SnCl_4$	Density (d) (in g/cc)			Viscosity (η) (in cp)			Specific electrical conductivity x · 10^4 ($ohm^{-1}cm^{-1}$)		
	20°	40°	60°	20°	40°	60°	20°	40°	60°
0.00	0.8558	0.8356	0.8171	0.790	0.560	0.436	Nonconducting		
9.47	0.9219	0.9015	0.8821	1.026	0.737	0.571	0.139	0.154	0.204
14.95	—	—	—	1.281	0.893	0.678	1.20	1.39	1.69
19.74	0.9925	0.9727	0.9527	1.569	1.062	0.818	2.44	3.19	4.15
25.08	1.0304	1.0091	0.9892	1.860	1.248	0.922	3.22	4.56	5.93
27.84	—	—	—	1.951	1.302	0.961	3.58	5.11	6.71
29.64	1.0601	1.0343	1.0170	2.029	1.329	0.974	3.58	5.12	6.72
31.97	—	—	—	2.020	1.304	0.948	3.30	4.82	6.26
33.13	1.0818	1.0591	1.0373	1.998	1.291	0.933	3.00	4.40	5.74
35.00	—	—	—	1.934	1.260	0.919	2.67	4.00	5.22
37.71	—	—	—	—	—	—	2.29	3.39	4.33
39.63	—	—	—	—	—	—	2.09	3.07	4.01
39.97	—	—	—	1.765	1.178	0.867	—	—	—
48.00	1.1497	1.1249	1.1014	1.468	1.008	0.757	—	—	—
49.38	—	—	—	—	—	—	1.14	1.58	1.91
60.10	1.1996	1.1739	1.1487	1.103	0.786	0.605	0.507	0.604	0.642
78.46	1.2737	1.2448	1.2177	0.795	0.600	0.476	Nonconducting		
100.00	1.3548	1.3229	1.2925	0.614	0.485	0.392	Nonconducting		

TABLE 2

Mole %, $SnCl_4$	Density (d) (in g/cc)			Viscosity (η) (in cp)			Specific electrical conductivity x · 10^4 ($ohm^{-1}cm^{-1}$)		
	20°	40°	60°	20°	40°	60°	20°	40°	60°
0.00	0.8537	0.8346	0.8160	0.871	0.629	0.486	Nonconducting		
9.87	0.9202	0.9002	0.8810	1.167	0.830	0.632	0.0673	0.0779	0.113
20.02	1.0053	0.9857	0.9654	1.552	1.060	0.815	1.21	1.49	1.96
24.89	—	—	—	2.178	1.433	1.038	2.46	3.47	4.74
27.76	—	—	—	2.322	1.511	1.108	2.70	3.82	5.05
30.10	—	—	—	2.327	1.498	1.092	2.67	3.78	4.90
30.62	1.0558	1.0338	1.0135	—	—	—	—	—	—
31.42	—	—	—	2.328	1.502	1.084	2.64	3.78	4.92
34.74	—	—	—	2.195	1.392	1.033	2.23	3.22	4.16
39.75	1.1028	1.0800	1.0567	1.872	1.238	0.923	1.60	2.30	3.01
49.77	1.1472	1.1235	1.1006	1.421	0.988	0.750	0.927	1.21	1.42
59.41	1.1884	1.1637	1.1399	1.191	0.853	0.653	0.473	0.548	0.562
79.72	1.2742	1.2457	1.2181	0.805	0.606	0.478	Nonconducting		
100.00	1.3548	1.3229	1.2925	0.614	0.485	0.392	Nonconducting		

As a result, the diagrams of the physicochemical analysis of the systems $SnCl_4$ – n-C_4H_9OH – C_6H_6 and $SnCl_4$ – n-$C_5H_{11}OH$ – C_6H_6 testify to the reaction of stannic chloride with these alcohols, leading to the formation of the compounds $SnCl_4 \cdot 2ROH$ and $SnCl_4 \cdot 3ROH$. The appearance of electrical conductivity in these systems is due to the formation of the compounds $SnCl_4 \cdot 3ROH$, which dissociate electrolytically into the two ions $[SnCl_4(RO)_2]H^-$ and ROH_2^+ [2, 3].

In Fig. 3 we have compared the isotherms of the corrected electrical conductivity of the systems $SnCl_4$ – C_2H_5OH [1], $SnCl_4$ – C_3H_7OH [1], $SnCl_4$ – C_4H_9OH and $SnCl_4$ – $C_5H_{11}OH$ at 40°, and also when diluted with 70 mole% of benzene. The isotherms of the corrected electrical conductivity fall on the graph in a regular manner: the highest is the isotherm relating to the system $SnCl_4$ – C_2H_5OH (Curve I), and the lowest is the isotherm of the corrected electrical conductivity of the system $SnCl_4$ – $C_5H_{11}OH$ (Curve IV); in other words, the corrected electrical conductivity decreases in a regular manner in going from C_2H_5OH to $C_5H_{11}OH$. This indicates that the extent of acid-base reaction decreases with increase in the length of the alcohol radical. An examination of Fig. 3 reveals a gradual

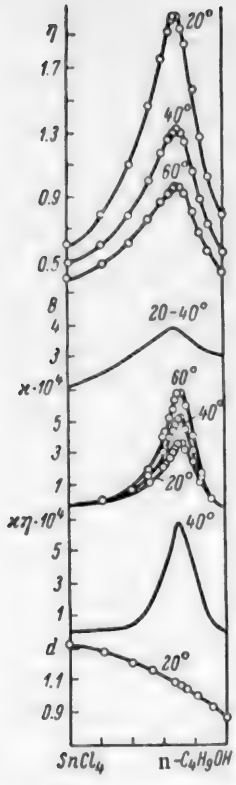

Fig. 1. Property–composition diagrams of systems $SnCl_4$ – n-C_4H_9OH.

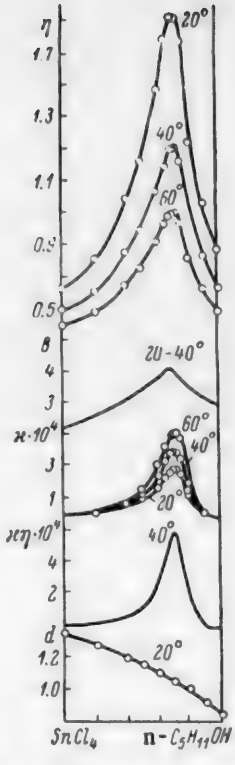

Fig. 2. Property–composition diagrams of systems $SnCl_4$ – n-$C_5H_{11}OH$.

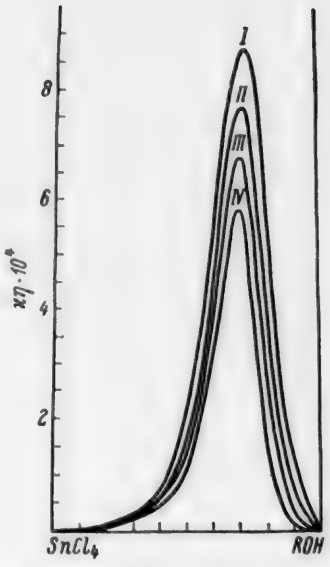

Fig. 3. Isotherms of corrected electrical conductivity of the systems: $SnCl_4$ – C_2H_5OH (I), $SnCl_4$ – C_3H_7OH (II), $SnCl_4$ – C_4H_9OH (III), and $SnCl_4$ – $C_5H_{11}OH$ at 40°, and when diluted with 70 mole % of benzene.

shift in the positions of the maxima toward the ordinate of the compound $SnCl_4 \cdot 2ROH$ when going from C_2H_5OH to $C_5H_{11}OH$: the maximum of the corrected electrical conductivity of the system $SnCl_4$ – C_2H_5OH is found at 25 mole% $SnCl_4$, of the system $SnCl_4$ – C_3H_7OH at 27 mole % $SnCl_4$, of the system $SnCl_4$ – C_4H_9OH at 29 mole % $SnCl_4$, and of the system $SnCl_4$ – $C_5H_{11}OH$ at 30 mole % $SnCl_4$. Such a shift in the positions of the maxima of the corrected electrical conductivity also testifies to the fact that the extent of the secondary acid-base reaction of $SnCl_4 \cdot 2ROH$ with ROH decreases in going from C_2H_5OH to $C_5H_{11}OH$, i.e., this shift is caused by a displacement of the equilibrium to the left, toward the formation of the complex acid $SnCl_4 \cdot 2ROH$.

$$[SnCl_4(RO)_2]H_2 + ROH \rightleftharpoons [SnCl_4(RO)_2]H^- + ROH_2^+$$

A similar rule is observed in the behavior of the monocarboxylic acids and their esters toward tin halides [4-8].

SUMMARY

1. A study was made of the electrical conductivity, viscosity and density of the systems $SnCl_4$ – n-C_4H_9OH – C_6H_6 and $SnCl_4$ – $C_5H_{11}OH$ – C_6H_6 at 20, 40 and 60°. The existence of the compounds $SnCl_4 \cdot 2ROH$ and $SnCl_4 \cdot 3ROH$ was established.

2. It was shown that the extent of secondary acid-base reaction of $SnCl_4 \cdot 2ROH$ with ROH decreases as the length of the alcohol radical increases.

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COMPLEX COMPOUNDS OF $SnCl_4$ and $SnBr_4$ WITH DIMEDON AND TERPINEOL

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Original article submitted March 21, 1960

Earlier we had obtained the complexes of stannic chloride and stannic bromide with cineole of composition $SnX_4 \cdot 2C_{10}H_{18}O$. Here it was found that the compound $SnBr_4 \cdot 2C_{10}H_{18}O$ possesses some interesting properties [1]. Because of this we made a study of the reaction of stannic bromide and stannic chloride with terpineol and with dimedon.

EXPERIMENTAL

Stannic chloride and the bromide were purified as described earlier [1]. Analytically pure dimedon was recrystallized 3 times from alcohol. The dimedon had m.p. 147, while the literature gives 147-149°. The terpineol, synthesized from terpinol hydrate, had the following constants:

d^{20}_{20} 0.9346, n^{20} 1.4824; literature data for dl-α-terpineol: d^{20}_{20} 0.935, $n^{20}D$ 1.4827 (1.4819), for β-terpineol: d^{20}_{20} 0.919, $n^{20}D$ 1.4747.

A comparison of the literature data with our results show that the compound obtained by us was α-terpineol. The acetic acid was purified by the fractional freezing of analytically pure acetic acid, and then it was distilled. The acetic acid had f.p. 16.6°, as compared to the literature value of 16.65°. The benzene was carefully purified in conventional manner, distilled, and then subjected to fractional freezing. The benzene had m.p. 5.5°, which corresponds to the literature data.

1. The complex compound of $SnCl_4$ with dimedon was obtained in acetic acid, since dimedon is difficultly soluble in stannic chloride, benzene, toluene, etc.

Viscous solutions were obtained when stannic chloride was mixed with dimedon in CH_3COOH (taken in the proportions of 1 mole of stannic chloride to either 1 or 2 moles of dimedon). The mixtures stratified when benzene was added. Repeated washing of the lower viscous layers with hot benzene, followed by removal of the benzene in a vacuum-desiccator, gave glassy materials with a greenish-yellow color.

The results of analyzing these products for tin and chlorine are given below.

Mixture of 1 : 1 Composition

Found %: Sn 23.84, 23.70, 23.48, 23.68, 23.85; Cl 26.85, 27.06, 27.44, 27.03. $SnCl_4 \cdot C_{10}H_{18}O$. Calculated %: Sn 29.63; Cl 35.39.

Mixture of 1 : 2 Composition

Found %: Sn 19.42, 19.44; Cl 23.68, 23.13. $SnCl_4 \cdot 2C_{10}H_{18}O$. Calculated %: Sn 21.94; Cl 26.22.

The analysis results come closest to the compound $SnCl_4 \cdot 2C_{10}H_{18}O$. The deviations in the amounts of tin and chlorine from theory are explained by the difficulty of removing the impurities from the glassy reaction products. However, our results unequivocally indicate the formation of the compound $SnCl_4 \cdot 2C_{10}H_{18}O$. The compound is difficultly soluble in nonpolar organic solvents, and does not conduct an electric current.

2. The complex compound of $SnBr_4$ with dimedon was obtained by mixing the components (in the ratio of 1 mole of stannic bromide to either 1 or 2 moles of dimedon) in the absence of a solvent. The mixtures were heated until all of the dimedon had dissolved. After repeated washing with hot benzene, followed by removal of the latter, the mixtures represented glassy products with a yellow-orange color.

The analysis results of these products are given below.

Mixture of 1 : 1 Composition

Found %: Sn 14.97, 14.95, 14.90; Br 39.66, 39.87. $SnBr_4 \cdot C_8H_{12}O_2$. Calculated %: Sn 20.52; Br 55.25.

Mixture of 1 : 2 Composition

Found %: Sn 15.86, 15.95, 15.68; Br 42.26, 42.26, 42.73. $SnBr_4 \cdot 2C_8H_{12}O_2$. Calculated %: Sn 16.51; Br 44.47.

The analysis results of the reaction products indicate that in both cases we obtained the complex compound $SnBr_4 \cdot 2C_8H_{12}O_2$. The low amount of tin and bromine in the glassy products when compared to theory for the compound $SnBr_4 \cdot 2C_8H_{12}O_2$ is explained by the fact that here, the same as in the case of stannic chloride, it proved impossible to remove all of the benzene from the glassy substances.

As a result, these data testify to the formation of the compound $SnBr_4 \cdot 2C_8H_{12}O_2$. This compound, the same as the complex of dimedon with stannic chloride, is difficultly soluble in organic solvents and does not conduct an electric current.

3. The complex compounds of $SnCl_4$ and $SnBr_4$ with terpineol were not isolated in the free state. The mixing of stannic chloride or stannic bromide with terpineol resulted in the evolution of heat and the formation of reaction products that represented viscous dark-brown liquids. After some time crystals appeared, the isolation of which from the viscous liquid proved impossible. Consequently, to establish the composition of the compounds of stannic chloride and stannic bromide with terpineol we employed the cryoscopic method [2-4]. We made both the direct and the reverse cryoscopic titration of stannic chloride and stannic bromide with terpineol. These results

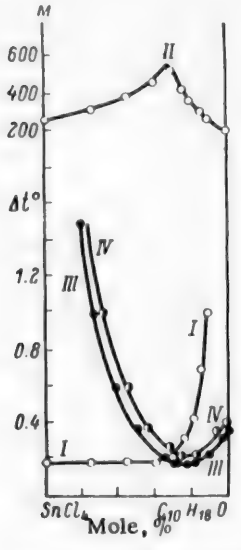

Fig. 1. Curves for the cryoscopic titration of benzene solutions. I) Titration of stannic chloride with terpineol; III and IV) titration of terpineol with stannic chloride; II) dependence of the molecular weight on the composition.

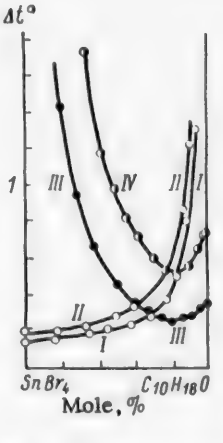

Fig. 2. Curves for the cryoscopic titration of benzene solutions. I and II) Titration of stannic bromide with terpineol; III and IV) titration of terpineol with stannic bromide.

are plotted in Figs 1 and 2. When constantly increasing amounts of terpineol are added to a solution of stannic chloride in benzene (Fig. 1, I) the depression remains nearly constant up to approximately 33 mole % stannic chloride, and then with further addition of terpineol a sharp increase in the depression is observed. Such a behavior of the depression indicates that stannic chloride forms the compound $SnCl_4 \cdot 2C_{10}H_{18}O$ with terpineol. That a compound of such composition is formed is also evidenced by the dependence of the molecular weight on the composition of the

system $SnCl_4$ – $C_{10}H_{18}O$ (Fig. 1, II). The curve, expressing this dependence, passes through a maximum at 33 mole % stannic chloride. The molecular weight, corresponding to the maximum, is equal to 550 while the formula molecular weight of the compound $SnCl_4 \cdot 2C_{10}H_{18}O$ is equal to 569.01.

In the reverse cryoscopic titration (Curve III), i.e., when stannic chloride is added to a solution of terpineol in benzene, the depression falls at first, reaches its minimum value at approximately 25 mole % stannic chloride, and then rises. The fall in the depression when stannic chloride is added to a solution of terpineol in benzene is caused by a deposition of the formed compound in the precipitate. The position of the minimum (25 mole % $SnCl_4$) indicates that in the concentration range, rich in terpineol, a third terpineol molecule adds, i.e., the compound $SnCl_4 \cdot 3C_{10}H_{18}O$ is formed, which dissociates electrolytically into 2 ions. The cryoscopic titration curve (Fig. 1, IV), relating to a more concentrated solution (with respect to benzene) than Curve III, also passes through a minimum, the position of which is found at 22-23 mole % $SnCl_4$. Such a shift of the minimum along the composition axis toward the terpineol side is probably explained by the formation, along with the compound of 1 : 3 composition, of the 1 : 4 compound. The compound $SnCl_4 \cdot 4C_{10}H_{18}O$ is also an electrolyte, which dissociates into 3 ions. These suppositions are supported by the fact that the system $SnCl_4$ – $C_{10}H_{18}O$ exhibits an electrical conductivity of the order of 10^{-5} ohm^{-1}cm^{-1}.

The behavior of terpineol toward stannic chloride is completely analogous to the behavior of other alcohols in this respect [5-7].

The results of the cryoscopic titration of stannic bromide with terpineol (Curves I and II) are shown in Fig. 2, as are also the results of the reverse titration of terpineol with stannic bromide (Curves III and IV). The shape of these curves is analogous to that obtained for stannic chloride, and consequently we will not describe them here. They testify to the formation of compounds of composition 1 : 2 and 1 : 4, and at the same time they show that the extent of reaction between stannic bromide and terpineol is less than in the case of stannic chloride. The solutions of stannic bromide in terpineol also conduct an electric current ($\varkappa = 10^{-5}$ ohm^{-1}cm^{-1}).

SUMMARY

1. The complex compounds of stannic chloride and stannic bromide with dimedon of composition $SnX_4 \cdot 2C_8H_{12}O_2$, where X = Cl or Br, were isolated. These complexes represent glassy substances, difficultly soluble in nonpolar organic solvents and soluble in CH_3COOH.

2. The existence of complex compounds of stannic chloride and stannic bromide with terpineol of composition $SnX_4 \cdot 2C_{10}H_{18}O$, $SnX_4 \cdot 3C_{10}H_{18}O$ and $SnX_4 \cdot 4C_{10}H_{18}O$, where X = Cl or Br, was established. Solutions of stannic chloride and stannic bromide in terpineol conduct an electric current. Creation of an electrical conductivity of the order of 10^{-5} ohm^{-1}cm^{-1} is associated with the dissociation of the compounds $SnX_4 \cdot 3C_{10}H_{18}O$ and $SnX_4 \cdot 4C_{10}H_{18}O$.

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COMPOUNDS OF TYPE $SnX_4 \cdot A \cdot B$

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Original article sumbitted March 21, 1960

Earlier [1-7] we had obtained complex compounds of type $SnX_4 \cdot 2A \cdot B$ and $SnX_4 \cdot 2A \cdot 2B$, in which different addenda were added in the inner and outer spheres. In this paper we present data indicating the existence of compounds of type $SnX_4 \cdot A \cdot B$.

In the literature we found the statement that A. Hantzsch and K. Meyer [8] obtained red complexes of composition $SnCl_4 \cdot C_{20}H_{14}O \cdot C_6H_5NO_2$, when stannic chloride was reacted with a solution of phenolphthalein in nitrobenzene. The compound $SnCl_4 \cdot CH_3NO_2 \cdot (CH_3)_3N$ was described in a recent paper [9]. Such compounds can be obtained by reacting tin halides with a mixture of two substances, the acid-base properties of which are not sharply different.

EXPERIMENTAL

$SnCl_4$, C_6H_5COOH, CH_3COOH, C_5H_5N, and $C_5H_{11}N$ were purified as described earlier [1, 2, 5]. "Pure" nitromethane was distilled over P_2O_5; b.p. 97.5° (697.3 mm). The composition of the compounds was established on the basis of the chemical analysis data, and in the cases where this was not possible, by cryoscopic titration [10].

1. The complex compound $SnCl_4 \cdot C_6H_5COOH \cdot CH_3COOH$ was obtained by the cautious reaction of stannic chloride with a solution of an equimolar mixture of acetic and benzoic acids in benzene (taken on the basis of 1 mole of stannic chloride to 2 moles of an equimolar mixture of acids). The crystals that deposited on standing were separated from the mother liquor, washed well with benzene, and analyzed for the amount of tin and chlorine. The results of analyzing the precipitates are given below.

Found %: Sn 26.83, 27.11, 26.82; Cl 32.82, 30.19, 30.92. $SnCl_4 \cdot CH_3COOH \cdot C_6H_5COOH$. Calculated %: Sn 26.81; Cl 32.03.

Calculation of the theoretical amount of tin and chlorine gives for the compound $SnCl_4 \cdot 2CH_3COOH$ in %: Sn 31.18; Cl 37.26; and for the compound $SnCl_4 \cdot 2C_6H_5COOH$ in %: Sn 23.51; Cl 28.09.

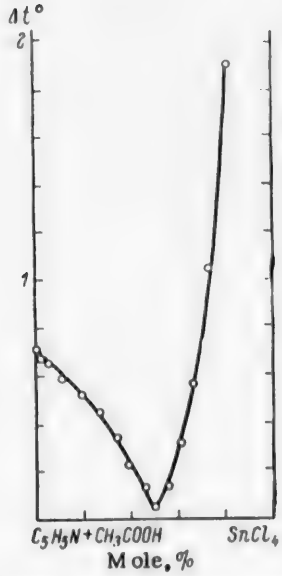
Judging from the analysis results, the precipitates can represent either the compound $SnCl_4 \cdot CH_3COOH \cdot C_6H_5COOH$ or an equimolar mixture of the complex acids $SnCl_4 \cdot 2CH_3COOH$ and $SnCl_4 \cdot 2C_6H_5COOH$. The last supposition can be rejected for the following reasons. The complex compound $SnCl_4 \cdot 2CH_3COOH$ is a clear viscous liquid at room temperature, readily soluble in benzene, whereas the complex compound $SnCl_4 \cdot 2C_6H_5COOH$ can be recrystallized from benzene and melts at 96.5°. Consequently, if our crystals were a mixture of compounds $SnCl_4 \cdot 2CH_3COOH$ and $SnCl_4 \cdot 2C_6H_5COOH$, then such a mixture after repeated washing with benzene should become enriched in compound $SnCl_4 \cdot 2C_6H_5COOH$, and the found amount of tin and chlorine in the precipitates should approach their amount in the compound $SnCl_4 \cdot 2C_6H_5COOH$, rather than in the equimolar mixture of complex acids. For this reason, the crystals isolated from the benzene solution are the compound $SnCl_4 \cdot CH_3COOH \cdot C_6H_5COOH$. This compound represents a dibasic complex acid with m.p. 81°.

2. The complex compound $SnCl_4 \cdot CH_3COOH \cdot C_5H_5N$ was obtained by the dropwise addition of stannic chloride to a homogeneous solution of an equimolar mixture of pyridine and acetic acid in benzene (taken on the basis of 1 mole of stannic chloride to 1 mole of pyridine and 1 mole of acetic acid). The precipitate was separated from the mother liquor, washed well with hot benzene, and dried over P_2O_5. The results of analyzing the precipitates are given below.

Found %: Sn 29.98, 30.08, 29.89, 30.28, 29.58, 29.56; Cl 35.37, 35.35, 35.25. $SnCl_4 \cdot CH_3COOH \cdot C_5H_5N$. Calculated %: Sn 29.69; Cl 35.48.

It can be seen from the analysis results that the amount of tin and chlorine in the precipitate corresponds to the compound $SnCl_4 \cdot CH_3COOH \cdot C_5H_5N$.

The results of the cryoscopic titration of an equimolar mixture of $CH_3COOH + C_5H_5N$ with stannic chloride in benzene solution are plotted on the graph in the form of a depression–composition diagram. From the graph it can be seen that as stannic chloride is added to the mixture of pyridine and acetic acid the depression of the melting point decreases clear down to 50 mole %, and then the further addition of stannic chloride causes it to increase. At the equivalent point, corresponding to 50 mole %, the depression is equal to 0.06°. This shape for the cryoscopic titration curve also indicates the formation of the compound of composition $SnCl_4 \cdot CH_3COOH \cdot C_5H_5N$. This compound is difficultly soluble in organic solvents, and melts at 128°.



Cryoscopic titration of mixture $C_5H_5N + CH_3COOH$ with stannic chloride in benzene solution.

3. The complex compound $SnCl_4 \cdot CH_3COOH \cdot C_5H_{11}N$ was obtained in the following manner. First we prepared the 1 : 1 compound of piperidine with acetic acid. A known weight of this compound was then added to a solution of stannic chloride in benzene solution, taken on the basis of 1 mole of stannic chloride to 1 mole of $C_5H_{11}N \cdot CH_3COOH$. The precipitate, obtained on long standing, was separated from the solution, washed with hot benzene, dried, and analyzed the amount of tin and chlorine. The results of analyzing the precipitates are given below.

Found %: Sn 28.64, 28.57, 28.55, 28.59, 28.53, 29.09, 29.35, 29.46, 28.87, 29.09, 29.27; Cl 35.25, 35.12, 35.11, 35.10, 34.60, 34.70, 34.84, 35.50, 35.07. 34.75, 35.07, 35.03. $SnCl_4 \cdot CH_3COOH \cdot C_5H_{11}N$. Calculated %: Sn 29.25; Cl 34.95.

The analysis results show that the precipitates represent the compound $SnCl_4 \cdot CH_3COOH \cdot C_5H_{11}N$. This compound is also difficultly soluble in organic solvents.

4. The complex compound $SnCl_4 \cdot CH_3NO_2 \cdot NH_2CH_2COOH$ was obtained by the reaction of stannic chloride with glycine in nitromethane solution (taken on the basis of 1 mole of stannic chloride to 1 mole of glycine in excess nitromethane). The solution on long standing deposited a precipitate of ammonium hexachlorostannate $[SnCl_6](NH_4)_2$. (Found %: Sn 32.11; Cl 57.36.) The filtrate was fractionally distilled in vacuo. An exceedingly viscous liquid remained in the distillation flask after the excess nitromethane had been removed. To reduce the viscosity, this liquid was diluted with benzene and on long stirring a crystalline precipitate was obtained, which was recrystallized in the same manner from nitromethane, washed well with benzene, and dried in a vacuum-desiccator over P_2O_5. The results of analyzing the precipitate are given below.

Found %: Sn 30.20, 30.30, 29.80, 30.02, 30.02, 30.21, 29.88, 30.30; Cl 35.30. 36.90, 35. 40, 36.13, 35.13, 34.45, 35.02, 34.79. $SnCl_4 \cdot CH_3NO_2 \cdot NH_2CH_2COOH$. Calculated %: Sn 29.96; Cl 35.76.

The analysis results show that the isolated crystals represent the complex compound $SnCl_4 \cdot CH_3NO_2 \cdot NH_2CH_2COOH$. This compound is readily soluble in nitromethane and acetic acid, and is difficultly soluble in nonpolar solvents; it deliquesces in the air.

SUMMARY

The following mixed complex compounds of type $SnCl_4 \cdot A \cdot B$ were obtained: $SnCl_4 \cdot CH_3COOH \cdot C_6H_5COOH$, $SnCl_4 \cdot CH_3COOH \cdot C_5H_5N$, $SnCl_4 \cdot CH_3COOH \cdot C_5H_{11}N$, $SnCl_4 \cdot CH_3NO_2 \cdot NH_2CH_2COOH$.

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MOLECULAR COMPOUNDS OF UROTROPINE

I. MOLECULAR COMPOUNDS OF UROTROPINE WITH SOME ORGANIC ACIDS IN AQUEOUS SOLUTIONS

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Original article submitted March 28, 1960

The presence of four tertiary nitrogen atoms in the urotropine [hexamethylenetetramine] molecule is responsible for the high activity of urotropine as a complexing agent. A number of urotropine compounds with organic substances of acid character, isolated by synthesis, is described in the literature. Thus, for example, molecular compounds of urotropine with tartaric, camphoric, trichloroacetic and picric acids are known, and also with phenol, pyrocatechol, resorcinol, hydroquinone, pyrogallol and phloroglucinol [1, 2]. However, only a few compounds of urotropine with organic acids can be isolated from solution, since urotropine in aqueous solutions, in the presence of acids, suffers hydrolysis when stored for a long time, heated, or subjected to dehydration. In connection with this, to study the reaction of urotropine with organic acids we resorted to one of the techniques of physicochemical analysis, namely, the Ostromisslensky–Job method [3, 4] of continuous changes.

In this paper we analyzed the materials that were obtained in studying the reaction of urotropine with different classes of acyclic acids. The following systems were studied: urotropine–formic acid–water, urotropine–acetic acid acid–water, urotropine–oxalic acid–water, urotropine–succinic acid–water, urotropine–malic acid–water, urotropine–tartaric acid–water, and urotropine–maleic acid–water (Table 1). The enumerated systems were studied on the basis of the density and refractive index data, and in some cases also on the basis of the specific electrical conductivity. The starting solutions were prepared from carefully dehydrated urotropine and acids of analytically pure grade, and contained 0.285 M of dissolved substance. The prepared acid solutions were mixed with the urotropine solution in different volume ratios, in such manner that the sum of the volumes remained constant (100 ml). The mixtures were shaken vigorously for 30 min, after which the density, refractive index and specific electrical conductivity were measured. The method used to make the measurements was described by us earlier [5]. All of the measurements were made at 20 + 0.05°.

The isotherms of the refractive index, specific electrical conductivity and deviations of the density from additivity are shown in Figs. 1-7. The deviations of the density from additivity were calculated using the equation

$$\Delta d = d_{\text{exp.}} - \frac{d_1 V_1 + d_2 V_2}{\Sigma V},$$

where: $d_{exp.}$ is the density of the solution, determined experimentally, d_1 and d_2 are the densities of the mixed solutions, V_1 and V_2 are their volumes, and ΣV is the sum of the volumes of the mixed solutions.

DISCUSSION OF THE RESULTS

In the systems urotropine–formic acid–water and urotropine–acetic acid–water (Figs. 1, 2) the deviations of the density from additivity are positive. The Δd isotherms pass through a maximum at 50 mole % urotropine; the isotherms of the refractive index and specific electrical conductivity are characterized by singular points at that ratio of the reactants where the formation in the systems of molecular compounds of composition $C_6H_{12}N_4 \cdot HCOOH$ and $C_6H_{12}N_4 \cdot CH_3COOH$ is indicated.

The isotherms of the properties, corresponding to the reaction of urotropine with the dicarboxylic acids: oxalic and succinic, are shown in Figs. 3 and 4. As can be seen from Fig. 3, in the system urotropine–oxalic acid–water the maximum of the deviations of the density from additivity and the point of break on the isotherms of the refractive

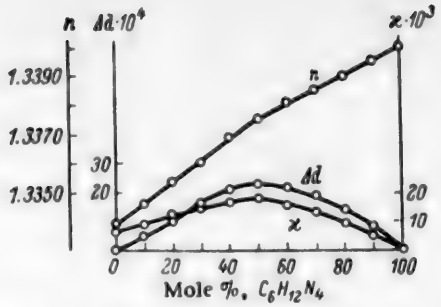

Fig. 1. System urotropine–formic acid–water.

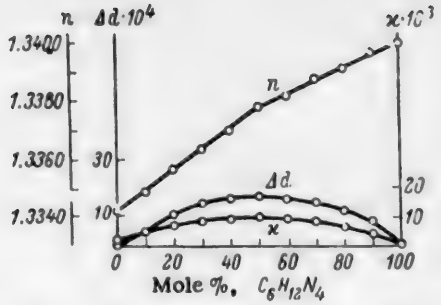

Fig. 2. System urotropine–acetic acid–water.

TABLE 1. Molecular Compounds of Urotropine with Some Acyclic Acids

System	Detected compounds
$C_6H_{12}N_4$–HCOOH–H_2O	$C_6H_{12}N_4 \cdot HCOOH$
$C_6H_{12}N_4$–CH_3COOH–H_2O	$C_6H_{12}N_4 \cdot CH_3COOH$
$C_6H_{12}N_4$–$H_2C_2O_4$–H_2O	$C_6H_{12}N_4 \cdot H_2C_2O_4$
$C_6H_{12}N_4$–$H_2C_2O_4$–H_2O	$2C_6H_{12}N_4 \cdot H_2C_2O_4$
$C_6H_{12}N_4$–$H_2C_4H_4O_4$–H_2O	$C_6H_{12}N_4 \cdot H_2C_4H_4O_4$
$C_6H_{12}N_4$–$H_2C_4H_4O_5$–H_2O	$C_6H_{12}N_4 \cdot H_2C_4H_4O_5$
$C_6H_{12}N_4$–$H_2C_4H_4O_6$–H_2O	$2C_6H_{12}N_4 \cdot H_2C_4H_4O_6$
$C_6H_{12}N_4$–$H_2C_4H_2O_4$–H_2O	$2C_6H_{12}N_4 \cdot H_2C_4H_2O_4$

index correspond to 67 mole % urotropine. The specific electrical conductivity curve has two break points, corresponding to 50 and 67 mole % urotropine. As a result, in the discussed system the isotherms of the properties indicate the formation of two compounds of composition $C_6H_{12}N_4 \cdot H_2C_2O_4$ and $2C_6H_{12}N_4 \cdot H_2C_2O_4$, the first of which appears only on the electrical conductivity isotherm. The isotherms of Δd and n, corresponding to the system urotropine–succinic acid–water, are characterized by singular points at an equimolecular ratio of the reactants. Consequently, succinic acid, in contrast to oxalic acid, forms with urotropine only one compound of composition $C_6H_{12}N_4 \cdot H_2C_4H_4O_4$.

The reaction of urotropine with multibasic hydroxy acids (malic and tartaric) is illustrated by Figs. 5 and 6. In the system urotropine–malic acid–water the maximum of the deviations of the density from additivity and the point of break on the isotherm of the refractive index correspond to a 1 : 1 molar ratio of urotropine to acid (Fig. 5) and indicate the formation of the compound $C_6H_{12}N_4 \cdot H_2C_4H_4O_5$. The singular points on the curves of the Δd, refractive index and specific electrical conductivity, characterizing the reaction of urotropine with tartaric acid (Fig. 6), correspond to 67 mole % urotropine and testify to the formation in the system of the compound $2C_6H_{12}N_4 \cdot H_2C_4H_4O_6$. The compound $C_6H_{12}N_4 \cdot H_2C_4H_4O_6$, prepared by the method of [6], could not be detected by physicochemical methods.

In the system urotropine–maleic acid–water the singular points on the isotherms of Δd and the refractive index indicate the formation of the molecular compound of composition $2C_6H_{12}N_4 \cdot H_2C_4H_2O_4$ (Fig. 7).

The detected molecular compounds of urotropine are summarized in Table 1.

In all of the studied systems the deviations of the density from additivity are positive, which is evidence of shrinkage in the system; the isotherm of the refractive index are turned by the break point away from the composition axis. As a rule, the curves of the specific electrical conductivity of the investigated systems pass through a maximum at the point corresponding to the composition of the compound (with the exception of the system urotropine–oxalic acid–water, which, apparently, is associated with the comparatively high electrical conductivity of oxalic acid solutions). Diagrams of this type correspond to reactions that proceed with the formation of ionogenic compounds from nonionogenic compounds or weakly dissociated substances. For this reason it is possible to assume

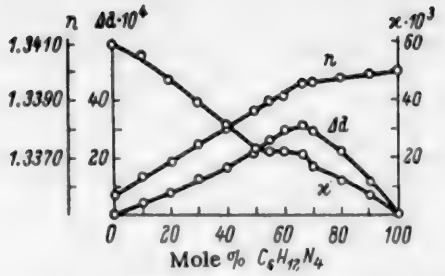

Fig. 3. System urotropine–oxalic acid–water.

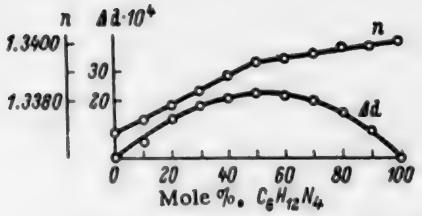

Fig. 4. System urotropine–succinic acid–water.

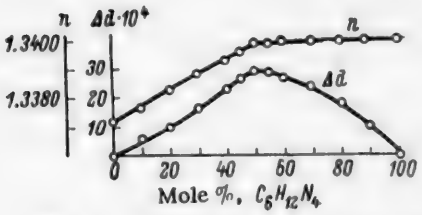

Fig. 5. System urotropine–malic acid–water.

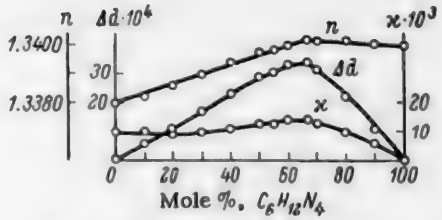

Fig. 6. System urotropine–tartaric acid–water.

that the reaction between urotropine and organic acids proceeds in accordance with the scheme:

$$Ur + HA \rightleftarrows UrH^{\cdot} + A', \tag{1}$$

where Ur and HA are arbitrary designations of the urotropine and acid molecule, respectively.

We also undertook the task of determining the instability constant of the complex ion $UrH^{\cdot}$.

If the acid reacting with urotropine is monobasic, then the equilibrium constant of reaction (1), assuming that the system obeys the law of mass action, is expressed by the equation

$$K_p = \frac{[UrH^{\cdot}]\,[A']}{[Ur]\,[HA]} \tag{2}$$

The instability constant K_i of the complex ion $UrH^{\cdot}$ is related to the equilibrium constant K_p by the equality

$$K_i = \frac{K_{HA}}{K_p},$$

where K_{HA} is the dissociation constant of the acid. To determine the equilibrium constants in the systems

TABLE 2. Values of the Equilibrium Constants in the System Urotropine–Formic Acid–Water at 20°

p	x	K_p	$K_i \cdot 10^4$
3.02	0.36	1.18	1.50
2.33	0.39	1.26	1.40
0.502	0.59	1.26	1.40
0.341	0.64	1.32	1.34

TABLE 3. Values of the Equilibrium Constants in the System Urotropine–Acetic Acid–Water at 20°

p	x	K_p	$K_i \cdot 10^4$
2.84	0.43	0.131	1.34
2.00	0.46	0.089	1.97
0.402	0.56	0.125	1.40

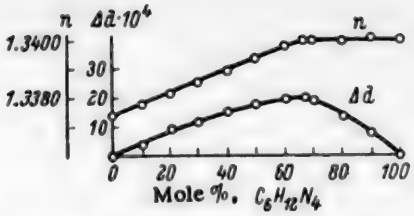

Fig. 7. System urotropine–maleic acid–water.

urotropine–formic acid–water and urotropine–acetic acid–water, we employed the Job method [4], which made it possible to calculate the equilibrium constant from the shift of the singular point on the isotherm of the properties when going from isomolar solutions to solutions with different molarity. When applied to reaction (1) the Job equation assumes the form:

$$K_p = \frac{p(1-2x)^2}{|(1+p)x-1|^2},$$

where p is the molar ratio of the mixed urotropine and acid solutions, and x is the volume fraction of the urotropine solution in the mixture corresponding to the singular point on the diagram.

The values of the equilibrium constants and of the instability constants of the UrH^+ ion, found from the shift of the singular points on the isotherms of the refractive index and of the deviations of the density from additivity, are compared in Tables 2 and 3. The dissociation constants of the formic and acetic acids were taken equal to 1.77×10^{-4} and 1.76×10^{-5}, respectively [7].

As can be seen from the data in Tables 2 and 3, the values of the instability constants of the UrH^+ ion vary within a comparatively narrow range. On the average the instability constant $K_i = (1.48 \pm 0.21) \times 10^{-4}$.

The average quadratic error is about 14% of the K_i value. The presence of a substantial average quadratic error is apparently due to the errors incurred in determining the positions of the singular point on the composition–property isotherms.

SUMMARY

1. Physicochemical analysis methods were used to study the reaction of urotropine with formic, acetic, oxalic, succinic, malic, tartaric, and maleic acids in aqueous solutions. The systems were studied on the basis of the refractive index, density and, in part, specific electrical conductivity data.

2. Eight molecular compounds of urotropine with the enumerated acids were detected.

3. The instability constant of the complex ion $[C_6H_{12}N_4H]^+$, determined by the Job method, is equal to $(1.48 \pm 0.21) \times 10^{-4}$.

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SPECTROSCOPIC INVESTIGATION OF THIONO-THIOL TAUTOMERISM

II. ULTRAVIOLET AND INFRARED ABSORPTION SPECTRA AND COMBINATION-SCATTERING SPECTRA OF SOLUTIONS OF THIOCARBAMIDE, PHENYLTHIOCARBAMIDE, DIPHENYLTHIOCARBAMIDE (ASYM.) AND DIPHENYLTHIOCARBAMIDE (SYM.)

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Earlier we showed [1] that in the crystalline state thiocarbamide and its phenyl derivatives exist in the thiono form; in the present work an attempt was made to answer the question as to whether molecules of the substances under investigation could undergo thionothiol tautomeric conversion in solution. It was of interest to us to learn the effect of the medium on the position of equilibrium, and the character of interaction of molecules of these substances in solution.

$$-NH-\underset{|}{C}=S \rightleftarrows -N=\underset{|}{C}-SH$$

It is well known that the presence of strong interaction of molecules of a dissolved substance with solvent molecules or among themselves, leading, for instance, to complex formation (appearance of new bonds) or to shifting of the equilibrium of mobile forms, may be established on the basis of investigation of the concentration (c) dependence of the molar extinction coefficient (ε), determined from the ratio

$$\varepsilon = \frac{1}{cd} \ln \frac{I_0}{I}$$

We investigated the UV-absorption and Raman spectra of thiocarbamide in water, acid (0.05 N HCl), and alkaline (0.05 N NaOH) solutions, and also the IR absorption spectra of solutions of thiocarbamide, phenylthiocarbamide, diphenylthiocarbamide (asym.), and diphenylthiocarbamide (sym.) in pyridine and acetone. The UV-spectra of the solution were measured in the 220-400 mμ region by means of an SF-4 spectrophotometer with a hydrogen lamp. The Raman spectra were obtained with a DFS-12 spectrometer (double monochromator with diffraction gratings).

The spectra of crystalline powders were obtained by means of a special cuvet consisting of a glass tube with a sealed-in glass cone. The substance was put into the space between the glass surfaces. The Raman spectra were excited by the λ 4358 A mercury line. As in the preceding work [1], the IR spectra of solutions of thiocarbamide and its phenyl derivatives in pyridine and acetone, were obtained in the 3600-500 cm^{-1} region with an IKS-11 single-beam spectrometer. Individual measurements in the 3600-2000 cm^{-1} region were additionally carried out with an IKS-14- double-beam spectrometer.

DISCUSSION OF THE RESULTS

a) Spectra of thiocarbamide in aqueous solution. The UV absorption spectra of thiocarbamide in aqueous solution were obtained at different concentrations in the range from 0.01 to 0.0001 M. The molar extinction coefficient $\varepsilon_{\lambda max}$ is 11700 (where λ_{max} is 236 mμ) and does not depend on the thiocarbamide concentration within the accuracy of measurement. This fact indicated the stability of thiocarbamide molecules in an aqueous medium, i.e., the absence of tautomeric conversion under these conditions. The spectra of neutral and alkaline solutions are

practically identical; in acid solution $\varepsilon_{\lambda\,max}$ is very slightly decreased (Fig. 1). This change apparently is due to interaction of the proton with amino groups. We did not find absorption maxima in the investigated region of the UV spectrum, other than that indicated above, in any case.

Our Raman spectra of crystalline thiocarbamide and its aqueous solutions, are schematically shown in Fig. 2. On the basis of literature data [2] (see also [1]), the lines found in the spectrum of crystalline thiocarbamide are interpreted in the following manner.

$\omega(cm^{-1})$	
3380 (3), 3286 (3), 3187 (3)	Valence vibrations $\nu(NH_2)$
1611 (1)	"Scissors" deformation vibrations $\delta(NH_2)$
1488 (1)	$\nu(-NH-\overset{\displaystyle S}{\overset{\displaystyle \vert}{C}}=S$
1386 (3)	Asymmetric valence vibrations ν_a (C-N)
1100 (7)	External deformation vibrations δ (NH)
736 (10)	Symmetric valence vibrations ν_c (C-N)
486 (6)	Skeleton vibrations $\delta\left(\begin{matrix}N\\N\end{matrix}\!\!>C=S\right)$

In the spectra of neutral, acid, and alkaline solutions of thiocarbamide, certain line shifts are observed in comparison with the spectrum of the crystalline substance. In the solutions, moreover, we could not detect NH_2-group vibration frequencies except $\omega = 1100\ cm^{-1}$. It is possible that in the region of valence vibrations they are simply masked by a broad, intense band belonging to associated water molecules; the line with frequency $\omega = 1611\ cm^{-1}$ has very low intensity and also was undetectable. Frequencies which could belong to the thiol form of thiocarbamide molecules, were not found either in the spectrum of crystalline thiocarbamide or in those of the solutions; in particular, no lines were found in the $2500\ cm^{-1}$ region (region of S-H valence vibration frequencies [3]). These data, as well as data on UV absorption spectra, indicate the great stability of the thiono form of thiocarbamide molecules in various media.

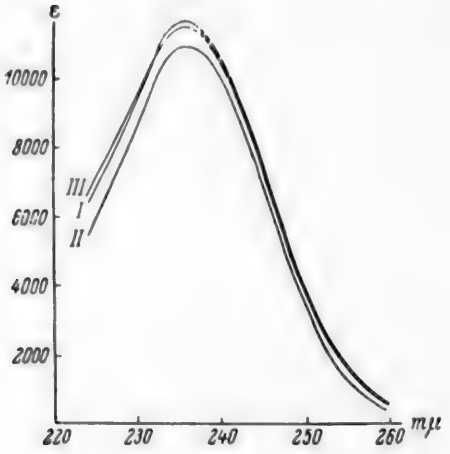

Fig. 1. UV absorption spectra of aqueous thiocarbamide solutions. I) Neutral solution; II) acid solution; III) alkaline solution.

b) IR absorption spectra of solutions of thiocarbamide and its phenyl derivatives in pyridine and acetone. The state of molecules of thiocarbamide and its phenyl derivatives, dissolved in pyridine and acetone, also may be determined by studying the corresponding characteristic absorption bands in the IR spectra [1] However, owing to the pronounced inherent absorption of pyridine and acetone it is impossible to trace through all the characteristic bands of molecules of the substances under investigation; therefore, for the most part, we shall consider only changes of spectra in the 3600-2000 cm^{-1} region, where absorption bands belonging to N-H and S-H vibrations, may be observed. In the intermediate-frequency region we were able to trace beyond the band $\delta\ (NH_2)\ \omega \sim 1590\text{-}1650\ cm^{-1}$.

Absorption bands of the investigated compounds and their solutions in the region of N-H valence vibrations, are schematically represented in Fig. 3. The great difference between the spectra of the crystalline and dissolved substances is striking: large shifts of the bands and in some cases even a change in their number. The latter makes it very difficult to interpret the results. However, taking into account that in no case did we observe S-H valence vibration bands or any other characteristic bands of the thiol form, it must be assumed first that the indicated changes in the spectra are determined not by tautomeric conversion, but by strong interaction of molecules of thiocarbamide and its derivatives in the thiono form with solvent molecules. This conclusion is confirmed by the presence of the band $\delta(NH_2)\ \omega\ 1590\ cm^{-1}$ in the spectrum of solution (III); the spectra of solutions (I) and (II) also contain this band, somewhat shifted toward the short-wave region.

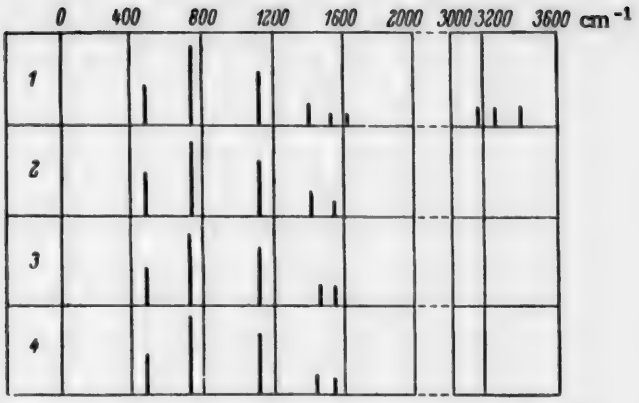

Fig. 2. Scheme of arrangement of Raman lines of thiocarbamide and its solutions. 1) Crystalline $CS(NH_2)_2$; 2) neutral 10% solution; 3) 5% solution in 0.1 N NaOH; 4) 5% solution in 1 N HCl.

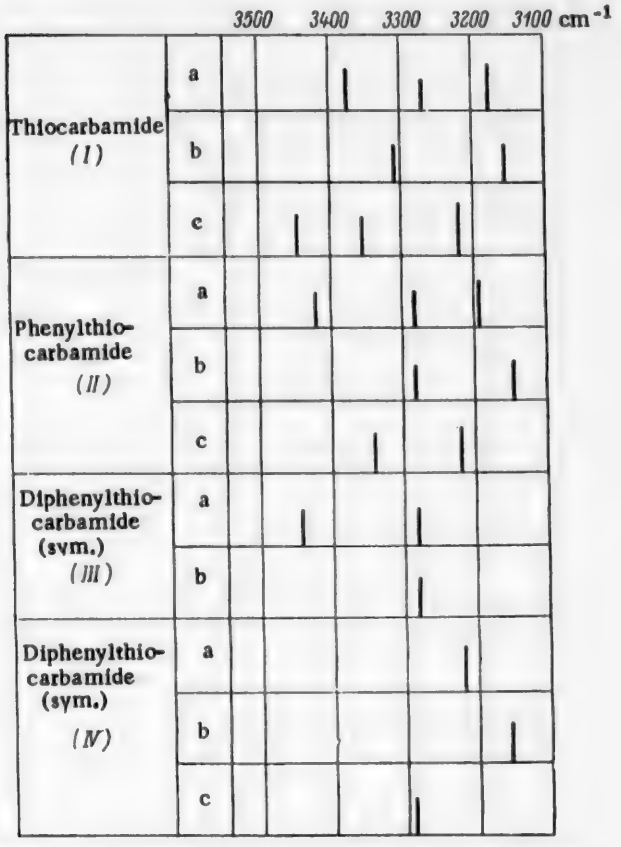

Fig. 3. Scheme of arrangement of the IR bands of amino-group valence vibrations. a) Crystalline; b) in pyridine; c) in acetone.

In pyridine the entire group of N-H valence-vibration bands is shifted toward lower frequencies in comparison with the crystalline substance, whereas in acetone the shift is in the opposite direction. This is especially well seen in the case of (IV), where only one band is observed in this region of the spectrum, and also in that of (I). From this

it follows that in pyridyne solutions of the investigated compounds, intermolecular hydrogen bonds are more pronounced than in the corresponding crystalline substances, whereas in acetone solutions they are less pronounced.

SUMMARY

1. The UV-absorption and Raman spectra of neutral (in the UV-region at various concentrations), acid, and alkaline aqueous solutions of thiocarbamide were investigated, as well as the IR-absorption spectra of solutions of thiocarbamide and its mono- and diphenyl derivatives in pyridine and acetone.

2. It was shown that in all media studied, the thiono form of molecules of thiocarbamide and its phenyl derivatives is stable, and tautomeric conversion does not occur. In pyridine solutions of the compounds investigated, intermolecular hydrogen bonds are more pronounced than in the crystalline state, whereas in acetone solution they are less pronounced.

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DENSITY, VISCOSITY, AND REFRACTIVE INDEX OF CERTAIN STRATIFIED BINARY LIQUID SYSTEMS

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Binary liquid systems having miscibility gaps at certain temperature and concentration limits, have not been fully studied by far. At best we know the binodal curve and lines of solubility of solid phases; the physical properties of systems above (or below) the consolute temperatures have scarcely been studied. However, just such investigations are necessary in order to determine the interaction of components, especially since the presence of stratification is often taken as a sign of weakened interaction of the substances in the system.

The wide application of physicochemical analysis to the study of the two-phase liquid state in ternary systems, which we undertook, required even more detailed knowledge of the nature of stratified binary systems. It was shown [1], that without proper allowance for the interaction of components of stratified binary systems which are themselves component parts of ternary ones, it is not possible to give an orderly theory of diagrams of state for such ternary systems. The results of experimental investigation of certain selected binary liquid systems with regard to density, viscosity, and refractive index, are set forth in the present article.

EXPERIMENTAL

In the work freshly-distilled compounds were used, whose physical constants agreed with reference-literature data. Density was determined in 3-5 ml pycnometers. Viscosity was measured in a closed-type Ostwald viscosimeter. On determining the densities and viscosities of the mixtures the temperature was kept constant with an accuracy within ± 0.1°. Refractive index was measured with an Abbe refractometer. Constancy of temperature of the prism and the liquid under investigation, was secured by continuous circulation of water from an ultrathermostat.

The n-Hexane – Nitrobenzene System*

This system was studied earlier with regard to the solubility of the liquid phases [2]. It has a stratification region with an upper consolute temperature; unlimited miscibility of nitrobenzene and hexane begins at 21°. We investigated this system with regard to the properties indicated above, at 30° (Table 1, Fig. 1).

The n-Hexane – Phenol System*

It is well known [3] that in the liquid state this system has a miscibility gap with an upper consolute temperature of 42.5°, above which the system components have unlimited solubility in one another. We obtained isotherms of the physical properties of the system for 55° (Table 2, Fig. 2).

Property isotherms of the hexane–nitrobenzene and hexane–phenol systems are similar to one another. They are lines, either convex toward the composition axis or slightly S-shaped; i.e., they indicate the absence of chemical interaction of the components. The negative deviation from additivity is due to the decomposition of associated molecules of nitrobenzene and phenol under the influence of the solvent.

The Isobutyric Acid – Water System**

This system has been studied experimentally several times with regard to the solubility of the liquid phases [4-6]. According to the data of various authors, the upper consolute temperature is 23.3-25.8°. The composition of the critical solution lies within the range 34-38 wt. % acid.

* Together with N. A. Torgashina.

** Together with A. D. Sheveleva, I. N. Sherstobitova, L. D. Orlova, and N. A. Samoilovskie.

TABLE 1. Density, Viscosity, and Refractive Index in the n-Hexane–Nitrobenzene System at 30°

Hexane content in the mixture (in mole %)	d	η	n_D
0.0	1.1928	1.6545	1.547
7.2	1.1048	1.3195	1.530
14.8	1.0405	1.0159	1.507
24.6	0.9781	0.8236	1.479
31.8	0.9109	0.6679	1.458
39.1	0.8645	0.5916	1.442
51.0	0.8037	0.4845	1.421
61.8	0.7562	0.4107	1.405
73.5	0.7181	0.3659	1.391
86.2	0.6833	0.3216	1.381
100.0	0.6501	0.3177	1.369

TABLE 2. Density, Viscosity, and Refractive Index in the n-Hexane–Phenol System at 55°

Hexane content in the mixture (in mole %)	d	η	n_D
0.0	0.0479	2.6991	1.533
9.2	0.9902	1.8585	1.527
18.6	0.9568	1.4523	1.520
28.2	0.9047	1.0685	1.508
37.9	0.8564	0.8254	1.479
48.3	0.8082	0.6280	1.460
57.9	0.7681	0.4869	1.428
68.1	0.7252	0.3697	1.406
78.5	0.6895	0.3190	1.383
89.1	0.6564	0.2836	1.366
100.0	—	0.2380	1.348

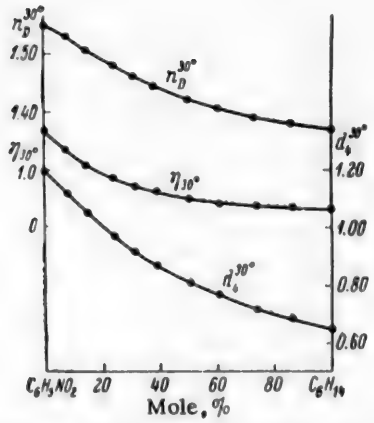

Fig. 1. Density (d), viscosity (η), and refractive index (n_D) isotherms of the n-hexane–nitrobenzene system.

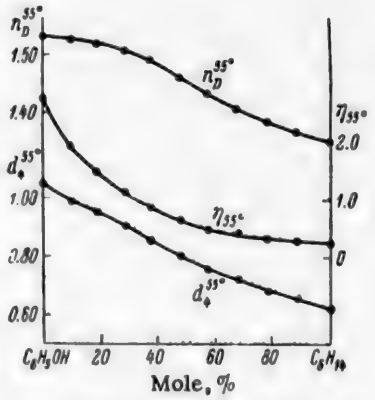

Fig. 2. Density (d), viscosity (η), and refractive index (n_D) isotherms of the n-hexane–phenol system.

We studied the system with regard to density, viscosity, and refractive index at 30° (Table 3, Fig. 3).

As is evident from Fig. 3, the density isotherm is a line, slightly convex toward the composition axis, which has a small maximum at 5 mole % acid. The viscosity isotherm passes through a maximum at 25 mole % acid. The refractive-index isotherm is a line markedly concave toward the composition axis.

The Phenylhydrazine – Water System*

This system was studied earlier with regard to the solubility of liquid and solid phases [7]. In the liquid state the system components give a miscibility gap with an upper consolute temperature of 55°. A phenylhydrazine hydrate having the composition $2C_6H_5NHNH_2 \cdot H_2O$ and melting congruently at 26.2°, was found by the melting-point method.

We investigated the density and viscosity of the system at 75° (Table 4, Fig. 4).

Both isotherms are curved lines, concave toward the composition axis and having slight inflection points between 60 and 70 mole % phenylhydrazine. The maximum deviation from additivity of the physical-property lines occurs at the composition $C_6H_5NHNH_2 \cdot H_2O$.

* Together with V. A. Shurov and T. A. Pirozhkova.

TABLE 3. Density, Viscosity, and Refractive Index in the Isobutyric Acid–Water System at 30°

Water content in the mixture (in mole %)	d	η	n_D
0.0	0.9407	1.12	1.3905
35.2	0.9589	1.51	1.3890
55.0	0.9702	2.12	1.3860
67.7	0.9783	2.43	1.3810
76.5	0.9847	2.51	1.3747
83.0	0.9895	2.42	1.3680
88.0	0.9937	2.00	1.3600
91.9	0.9971	1.58	1.3525
95.1	0.9985	1.28	1.3455
97.8	0.9982	1.02	1.3390
100.0	0.9957	0.80	1.3320

TABLE 4. Density and Viscosity in the Phenylhydrazine–Water System at 70°

Water content in the mixture (in mole %)	d	η
100.0	0.9760	0.406
90.1	1.0122	0.562
80.4	1.0304	0.753
70.0	1.0420	0.916
58.7	1.0483	1.051
50.6	1.0508	1.122
40.8	1.0516	1.162
23.0	1.0527	1.176
10.0	1.0560	1.216
0.0	1.0595	1.244

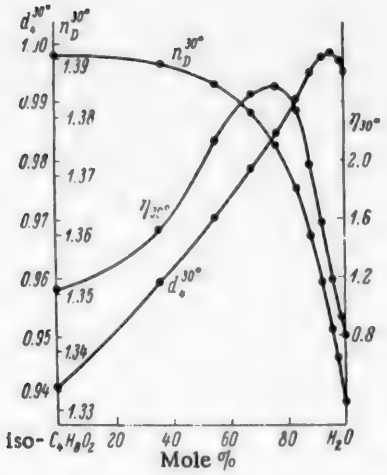

Fig. 3. Density (d), viscosity (η), and refractive-index (n_D) isotherms of the isobutyric acid–water system.

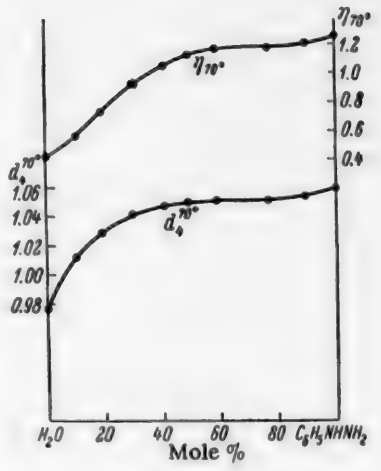

Fig. 4. Density (d) and viscosity (η) isotherms of the phenylhydrazine–water system.

The Triethylamine – Water System*

Contrary to that considered above, this system has a stratification region with a lower consolute temperature [2, 4, 8]. Unlimited miscibility in the system begins at 18.7°. We studied its density, viscosity, and refractive index at 5 and 15° (Table 5, Fig. 5).

The density isotherms are lines slightly convex toward the composition axis. The refractive-index isotherms, on the other hand, are concave toward the composition axis, with maximum deviation from additivity at 33 mole % triethylamine. The viscosity isotherms have pronounced maxima at approximately 10 mole % triethylamine.

In the last three systems: isobutyric acid–water, phenylhydrazine–water, and triethylamine–water, chemical interaction of the components definitely occurs. Products of mutual association of the components probably arise as a result of hydrogen-bond formation. However, all these irrational systems apparently contain several addition products which are thermally dissociated in the liquid phase. The noncorrespondence of the individual physical-property lines to the most probable compositions of the chemical compounds in the systems, is explained by association of

* Together with S. F. Kudryashov, G. S. Nikolaeva, and L. V. Voronova.

TABLE 5. Density, Viscosity, and Refractive Index in the Triethylamine–Water System at 5 and 15°

Water content in the mixture (in mole %)	d		η		n_D	
	5°	15°	5°	15°	5°	15°
0.0	0.7400	0.7312	0.4922	0.4688	1.4100	1.4039
10.0	0.7501	0.7406	0.5802	0.5189	1.4120	1.4065
20.1	0.7603	0.7512	0.6728	0.5922	1.4127	1.4080
30.2	0.7704	0.7609	0.8486	0.7137	1.4127	1.4080
39.8	0.7821	0.7732	1.1639	0.9263	1.4127	1.4078
49.7	0.7964	0.7867	1.6755	1.2560	1.4125	1.4075
59.3	0.8142	0.8043	2.5065	1.7234	1.4090	1.4050
72.1	0.8479	0.8299	5.4624	3.1722	1.4060	1.4025
80.0	0.8746	0.8626	7.3604	4.1811	1.3990	1.3950
90.0	0.9239	0.9145	7.9896	4.5483	1.3780	1.3770
100.0	0.9999	0.9991	1.5160	1.1410	1.3335	1.3334

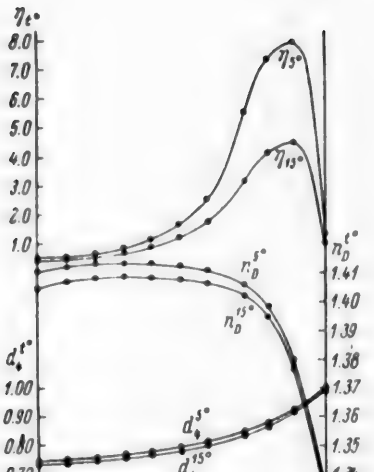

Fig. 5. Density (d), viscosity (η), and refractive-index (n_D) isotherms of the triethylamine–water system.

molecules of the components: As a rule, stratified binary liquid systems contain one or both components in the associated state; decomposition of the associated molecules under the influence of the second substance, leads to distortion of the character of the physical-property lines.

Our observations support the point of view, advanced earlier [1], that a miscibility gap with an upper consolute temperature may be encountered both in binary systems whose components interact chemically, and in systems in which the interrelation of components is close to normal, especially beyond the limits of the consolute temperatures. Chemical interaction of components always occurs in stratifying binary systems with a lower consolute temperature. Physical-property isotherms of the triethylamine–water system confirm this. A detailed test of the hypotheses considered above, would require further experimental work, other homogeneous liquid systems being investigated and a greater number of possible physical properties being studied.

SUMMARY

1. The binary systems nitrobenzene–n-hexane, phenol–n-hexane, isobutyric acid–water, and triethylamine–water were studied with regard to density, viscosity, and refractive index and the phenylhydrazine–water system, with regard to density and viscosity. Physical-property isotherms of the first two systems correspond to systems whose components do not interact chemically; it was found that in the other three systems the components do so interact.

2. The isobutyric acid–water, phenylhydrazine–water, and triethylamine–water systems are irrational in character and apparently contain several addition products.

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PHYSICOCHEMICAL ANALYSIS OF SYSTEMS CONTAINING SALTS OF ORGANIC ACIDS

III. RECIPROCAL SYSTEM OF POTASSIUM AND SODIUM BROMIDE AND ACETATES

I. I. Il'yasov and A. G. Bergman

Translated from Zhurnal Obshchei Khimii, Vol. 31, No. 2,
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Original article submitted October 1, 1960

In article I of this series [1], a phase diagram of the reciprocal system of potassium and sodium chlorides and acetates was shown. On transition from chlorides to bromides and iodides the reaction equilibrium shifts more and more toward sodium acetate and the potassium halide. Thus for bromides we have:

$$\underset{\underbrace{259.33\ \text{kcal}}}{\underset{173.3}{KOOCCH_3} + \underset{86.03}{NaBr}} \longrightarrow \underset{\underbrace{263.53\ \text{kcal}}}{\underset{169.80}{NaOOCCH_3} + \underset{93.73}{KBr}}$$

The exothermic heat effect of this reaction is 4.20 kcal/equiv. For chlorides, correspondingly, we obtain 2.44 kcal/equiv, and for iodides 5.97 kcal/equiv. The differences between the heat effects of the chloride, bromide, and iodide reciprocal systems, are: Br − Cl = 1.76 kcal, I − Br = 1.77 kcal. In the given case the secondary periodicity in the series Cl − Br − I, which we noted earlier [2], is absent.

In the reciprocal system Na, K ‖ F, CH_3COO the equilibrium is shifted toward the pair NaF, $KOOCCH_3$. The heat effect of the corresponding reaction is 5.04 kcal/equiv. Let us note that in all the many reciprocal systems containing sodium and potassium fluorides, NaF is always a component of the stable salt pair.

EXPERIMENTAL

The investigation was conducted by the method described earlier [1]. Melting points of the components: $NaOOCCH_3$ 328°, $KOOCCH_3$ 306°, NaBr 755°, and KBr 740°. The melts were stable up to 400°; above, slight decomposition began. In this system, therefore, we are limited to the 450° isotherm. All data on compositions are given in equivalent percent.

Binary Systems (Fig. 1)

1. $NaOOCCH_3$ − $KOOCCH_3$ [1, 3]. Forms an incongruently-melting compound of composition 1 : 2; the transition point lies at 255° and 65% $KOOCCH_3$.

2. $NaOOCCH_3$ − NaBr was studied by us. The eutectic was formed at 319° and 12.5% NaBr.

3. $KOOCCH_3$ − KBr was studied by us. The eutectic contained 10% KBr and crystallized at 290°.

4. NaBr − KBr [4]. Forms continuous solid solutions. According to our data, the minimum melting point (638°) lies at 52% KBr. On cooling, solid solutions persist down to room temperature, but then begin slowly to decompose.

The Reciprocal System Na, K ‖ Br, CH_3COO (Fig. 2)

Two diagonals and five internal sections were studied. The stable diagonal section is $NaOOCCH_3$ − KBr; a simple eutectic with m.p. 308° is formed at 12% KBr. The diagonal divides the square of the reciprocal system into two quasi-ternary systems: 1) $NaOOCCH_3$ − NaBr − KBr and 2) $NaOOCCH_3$ − KBr − $KOOCCH_3$. The diagonal NaBr − $KOOCCH_3$ is metastable. The univariant intersection point of the $KOOCCH_3$ and KBr branches lies at 275° and 9% NaBr. The intersection of the KBr and NaBr branches on this diagonal, lies above the temperature of stability of

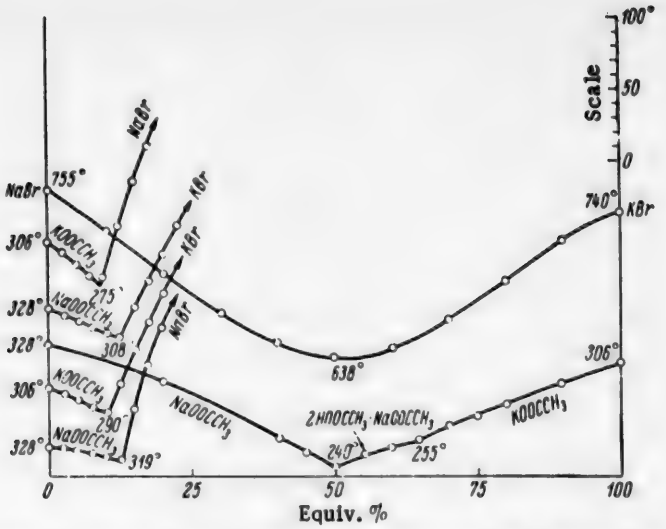

Fig. 1. Melting point curves of binary systems and diagonal sections of the reciprocal system Na, K ‖ Br, CH_3COO.

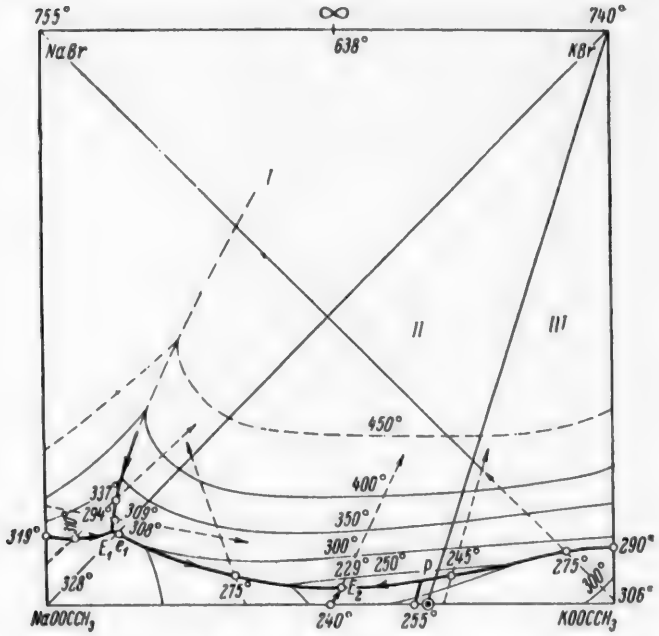

Fig. 2. Scheme of distribution of sections, and triangulation of the composition square of the reciprocal system Na, K ‖ Br, CH_3COO.

the melts. By means of the aggregate of all the internal sections, the crystallization field can be delineated and isotherms drawn up to 450°. The incongruently-melting compound $NaOOCCH_3 \cdot 2KOOCCH_3$, occupies a very small field, 0.9%, in the system; nevertheless, the cross section from the pole of the compound of acetates to KBr is a triangulating one. The field of NaBr – KBr continuous solid solutions splits into limited solid solutions of NaBr and KBr at about 400-450°, whereas in the binary system they come to room temperature without decomposing. Owing to this a triple eutectic point is formed at 294° inside the triangle $NaOOCCH_3$ – NaBr – KBr.

Position of Triple Invariant Points

Point	Temp.	Composition (in mole %)				Equilibrium phases
		$NaOOCCH_3$	KBr	NaBr	$KOOCCH_3$	
E_1	294°	88.0	10.5	1.5	—	$NaOOCCH_3$—KBr—NaBr
e_1	308	88.0	12.0	—	—	$NaOOCCH_3$—KBr
E_2	225	48.5	3.0	—	48.5	$NaOOCCH_3$—KBr—$NaOOCCH_3 \cdot 2KOOCCH_3$
P	245	34.5	3.0	—	62.0	$NaOOCCH_3 \cdot 2KOOCCH_3$—KBr—$KOOCCH_3$

Thus, whereas the system Na, K ‖ Cl, CH_3COO is a reversible-reciprocal one with the principal triangulating diagonal $NaOOCCH_3$—KCl, the system Na, K ‖ Br, CH_3COO, owing to its greater conventional heat of exchange, is an irreversible-reciprocal one in which a small ridge is formed along the stable diagonal $NaOOCCH_3$—KBr. The curve limiting the NaBr field was drawn by us arbitrarily, up to its intersection with the metastable diagonal NaBr—$KOOCCH_3$ (Fig. 2). On comparison of the bromide system with the corresponding chloride one we note that bromides are somewhat more soluble in acetate melts. The readily-fusible melts of this system may be used as electrolytes.

SUMMARY

1. The reciprocal system of potassium and sodium bromides and acetates was investigated.

2. Owing to its great conventional heat of exchange, the system belongs to the irreversible-reciprocal type. The diagonal $NaOOCCH_3$—KBr is stable.

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All abbreviations of periodicals in the above bibliography are letter-by-letter transliterations of the abbreviations as given in the original Russian journal. *Some or all of this periodical literature may well be available in English translation.* A complete list of the cover-to-cover English translations appears at the back of this issue.

DIPOLE MOMENTS OF o- AND p-ISOBORNYL CRESOLS AND THEIR BROMIDES

I. Yu. Kokoreva and V. M. Kazakova

M. V. Lomonosov Moscow Institute of Fine-Chemical Technology
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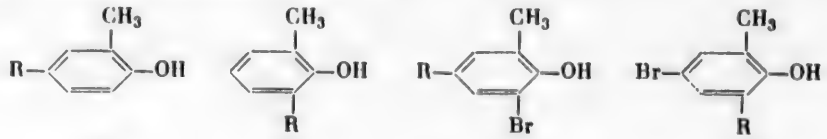
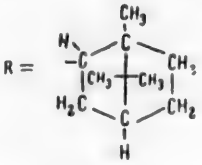
Original article submitted January 29, 1960

To confirm the proposed structure we measured the dipole moments of four compounds: p-isobornyl cresol (I), o-isobornyl cresol (II) and their bromides (III) and (IV).



(I) (II) (III) (IV)

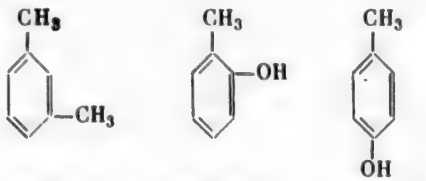


The dielectric permeabilities were measured by the heterodyne method in dilute benzene solutions at 25°. The dielectric polarizations were extrapolated to infinite dilution by the Hedestrand method, the refractions were calculated by the refractions of the bonds. The results obtained are given in the table.

Total Polarization P_∞, Refraction P_{el}, Orientation Polarization P_{or} and Dipole Moment μ (in D)

Name	P_∞	P_{el}	P_{or}	μ
p-Isobornyl cresol (I)	118.9	74.2	44.7	1.46
o-Isobornyl cresol (II)	117.8	74.2	43.6	1.44
Bromide of p-isobornyl cresol (III)	152.9	82.0	70.9	1.84
Bromide of o-isobornyl cresol (IV)	245.9	82.0	163.9	2.80

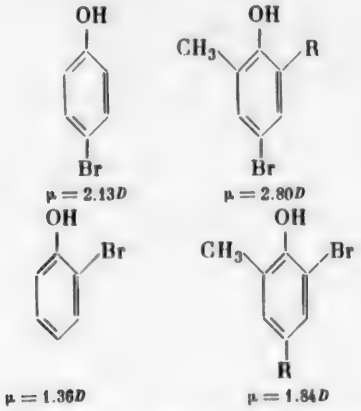
As may be seen from the data of the table, the dipole moments of (I) and (II) are practically the same. This is not surprising because a comparison of the dipole moments of m-xylene and of o- and p-cresols shows that these values can be expected to be similar.



$\mu = 0.40D$, $\mu = 1.41D$, $\mu = 1.57D$.

It may evidently be assumed that the polarity of the isobornyl radical is practically the same as that of the methyl group, because the dipole moment of borneol (1,59 D) [1] is close to the dipole moment of aliphatic alcohols.

For the bromides of p- and o-isobornyl cresols the dipole moment values obtained also correspond exactly to the values which may be assumed from the structure of these molecules. That the position of Br with respect to the OH group has been determined correctly in these compounds is confirmed by a comparison of the dipole moments of (III) and (IV) with the dipole moments of o- and p-bromophenols [2].



The authors wish to express their thanks to L. A. Kheifits, L. M. Shulov and V. N. Belov for supplying the compounds for these measurements.

SUMMARY

1. The dipole moments of o- and p-isobornyl cresols and their bromides were measured.

2. The structures of o- and p-isobornyl cresols and their bromides were confirmed by means of dipole moments.

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THE VALUES OF THE ISOBARIC-ISOTHERMIC POTENTIAL AND THE ACTIVITY PRODUCT OF $Ni(OH)_4$

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Translated from Zhurnal Obshchei Khimii, Vol. 31, No. 2,
pp. 372-374, February, 1961
Original article submitted June 3, 1959

Ferric, cobaltic and nickelic hydroxides play an important role in hydrometallurgy and other branches of industry. For this reason there is a constant flow of reports dealing with the development of the experimental technique of the determination of different physicochemical constants of these substances, including revised results of these determinations. The most essential difficulties are met with during the investigation of cobaltic [1] and nickelic [2] hydroxides. This is understandable because these compounds have extremely high oxidizing properties and under ordinary conditions can oxidize a great many substances and decompose water [3]. In our report [2], the value of the normal redox potential of $Ni^{2+}/Ni(OH)_4$ was determined theoretically on the basis of the literature data available at that time on the relation between the potential of $Ni(OH)_4$ at a nickel electrode, on the one hand, and the pH of the solution and the solubility product of nickelous hydroxide, on the other. The calculation gave the value +1.93 v, instead of the former value $E^0 = +1.68$ v, calculated by Latimer [3]. There are presently available new data, according to which the activity product of nickelous hydrate is $1.36 \cdot 10^{-15}$ [4] or $3.6 \cdot 10^{-16}$ [5], which differ considerably from Gayer and Garret's value of $6.5 \cdot 10^{-18}$ [6] used in our calculation. If the data of [4] and [5] are accepted, the redox potential of the system $Ni^{2+}/Ni(OH)_4$ is about +2.04 v. It may therefore be assumed with fair certainty that the normal redox potential of the process

$$Ni^{2+} + 4H_2O = Ni(OH)_4 + 4H^+ + 2e^- \qquad (1)$$

is between 1.93 and 2.04 v, i.e., being one of the strongest oxidizers, the hydroxide of tetravalent nickel is—as we have previously [3] indicated—very unstable. Its instability is explained both by its capacity to decompose water and to oxidize hydroxyl ions combined with an Ni^{4+} ion in an $Ni(OH)_4$ molecule

$$Ni(OH)_4 = Ni(OH)_2 + H_2O + \frac{1}{2}O_2 \qquad (2)$$

In view of its specific properties, the activity product of $Ni(OH)_4$ cannot be determined directly. We therefore made attempts to determine this value theoretically, via the isobaric-exothermic potential (free energy) of formation of $Ni(OH)_4$.

The free energy of process (1) is: $\Delta Z^0 = -23060nE^0 = -\begin{Bmatrix}-2.04 \cdot 2 \cdot 23060\\-1.93 \cdot 2 \cdot 23060\end{Bmatrix} = \begin{Bmatrix}+94000\\+89000\end{Bmatrix}$ cal

i.e., a mean value of +91500 ± 2500 cal; therefore, assuming, according to [3], that ΔZ^0: Ni^{2+} is −11.53 kcal, H_2O is −56.69 kcal and H^+ 0.0 kcal, we obtain, in accordance with equation (1): $\Delta Z^0_{Ni(OH)_4} = (-11.53) + 4(-56.69) - (+91.50 \pm 2.50) = -329.79 \pm 2.50$ kcal/mole.

The value obtained corresponds to the formation of $Ni(OH)_4$ from the elements. To calculate the activity product of $L_{Ni(OH)_4}$ it is necessary to know the value of ΔZ^0 of the formation of $Ni(OH)_4$ according to the reaction:

$$Ni^{4+} + 4(OH^-) \rightleftarrows Ni(OH)_4 \text{ sol.} \qquad (3)$$

At present, only an approximate calculation of the value of $L_{Ni(OH)_4}$ can be given because the isobaric-isothermic potential of the formation of the Ni^{4+} ion is unknown. However, an analysis of the trends of the variation of ΔZ^0 with an increase of the positive charge in simple ions shows (according to literature data [3, 7]) that for the majority

of such ions the ΔZ^0 value of Ni^{4+} may be expected to be near zero or in the region of positive values, with an absolute value of the order of several tenths, within the over-all limits of 100 kcal/g-ion. Therefore the above-obtained value of $\Delta Z^0_{Ni(OH)_4}$ must be reduced, first, by $4\Delta Z^0_{OH^-} = 4(-37.6) = -150.4$ kcal and, secondly, by the value $\Delta Z^0_{Ni^{4+}} \approx 0 - 100$ kcal/mole, i.e., the value of $\Delta Z^0_{Ni(OH)_4}$ according to reaction (3) must lie between −180 and −280 kcal/mole. We assume that −180 kcal/mole is the more probable value.

Further, since the activity product is a constant of the equilibrium of the reverse reaction to (3), i.e., $L = \frac{1}{K}$, L can therefore be calculated from the known relation:

$$\Delta Z^0 = -RT \ln K = -RT \ln \frac{1}{L} = +1364.3 \log L$$

hence $\log L_{Ni(OH)_4} = -132 - -205$ or $L_{Ni(OH)_4} = 10^{-132} - 10^{-205}$, which indicates the negligibly small solubility of $Ni(OH)_4$.

SUMMARY

1. The isobaric-isothermic potential of the formation of $Ni(OH)_4$ from the elements was calculated.
2. An approximate calculation of the activity product of $L_{Ni(OH)_4}$ was made.

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THE ALKYLATION OF o-BROMOPHENOL BY PROPYLENE, PENTENE-1 AND PENTENE-2

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Continuing our investigations on the alkylation of halogenated phenols by olefins [1, 2], in the present work we studied the reaction of o-bromophenol with propylene, pentene-1 and pentene-2 in the presence of molecular compounds of boron fluoride with orthophosphoric acid and ethyl ether. As was shown by the investigations, in contrast to butene-2 [1], with these olefins o-bromophenol forms one ether and one phenolic product. Under certain conditions the latter are formed in higher yield than the ether compounds. The same compounds are obtained with pentene-1 and pentene-2. As may be seen from the results in the experimental section, the effect of the molar ratios of the reagents, temperature, and the amount and nature of the catalyst on the ratio of the ether and phenolic products of alkylation is shown particularly clearly in this reaction. The use of carbon tetrachloride as the solvent reduces considerably the yield of both phenolic and ether products. Thus, when o-bromophenol reacts with pentene-2 in the presence of $BF_3 \cdot O(C_2H_5)_2$ in CCl_4 at room temperature for 48 hr, 4-sec-amyl-2-bromophenol and the sec-amyl ether of 2-bromophenol are obtained with yields of 4.8 and 5.4%, respectively, while in the presence of $BF_3 \cdot H_3PO_4$ and under the same conditions the yields are 17.3 and 22.6%, respectively.

EXPERIMENTAL

The o-bromophenol necessary for the reaction was obtained by bromination of phenol and had a b.p. of 64-65° (3 mm), $n^{20}D$ 1.5863. Pentene-2 was separated from the waste products of the synthetic rubber industry [2]. Propylene and pentene-1 were obtained by dehydration of n-propyl and n-amyl alcohols over Al_2O_3. Pentene-1 had a b.p. of 31°, d^{20}_4 0.6410 and $n^{20}D$ 1.3712.

Alkylation of o-Bromophenol by Propylene in the Presence of $BF_3 \cdot H_3PO_4$

The reaction was investigated in the same way as that previously described for p-bromophenol [2]. Constant temperature was maintained by adjusting the rate at which propylene was passed into the o-bromophenol and the catalyst. For each experiment, 0.1 mole of propylene and corresponding amounts of o-bromophenol and $BF_3 \cdot H_3PO_4$ were used. The reaction mass, which was light-yellow liquid at the beginning of the reaction, became a dark-brown opaque oil towards the end of the latter. After a specific amount of propylene had been added the mixture was stirred for 2 hr at 18-20° and left overnight; it was then treated in the usual manner. The results of the experiments are given in Table 1.

Isopropyl ether of 2-bromophenol (I)—a colorless oily liquid with a pleasant odor.

B.p. 73° (2 mm), d^{20}_4 1.3220, $n^{20}D$ 1.5355, MR_D 50.64; calc. 49.56.

Found %: Br 37.03, 37.15. $C_9H_{11}OBr$. Calculated %: Br 37.17.

Simple isopropyl ether of salicylic acid. Obtained by substitution of an atom of bromine in (I) by a carboxylic group via organomagnesium synthesis, with a yield of 64.6%. It is a colorless oily liquid.

B.p. 135-136° (2 mm), d^{20}_4 1.1262, $n^{20}D$ 1.5275, MR_D 49.2; calc. 48.0.

Found %: M 181.1, 180.0. $C_{10}H_{12}O_3$. Calculated: M 180.2.

4-Isopropyl-2-bromophenol (II)—a colorless oily liquid with an odor of phenol.

B.p. 83-84° (3 mm), d^{20}_4 1.3770, $n^{20}D$ 1.5510, MR_D 49.82; calc. 49.44.

Found %: Br 37.36, 37.12. $C_9H_{11}OBr$. Calculated %: Br 37.17.

TABLE 1. Alkylation of o-Bromophenol by Propylene

Expt. No.	Molar ratios of bromophenol, propylene and $BF_3 \cdot H_3PO_4$	Reaction time (hr)	Alkylation products			
			isopropyl ether of 2-bromophenol		isopropyl-2-bromophenol	
			boiling range at 2 mm	yield (%)	boiling range at 2 mm	yield (%)
1	2 : 1 : 0.2	3.5	70—75	21.4	76—82	22.0
2	2 : 1 : 0.2	4.0	67—71	9.9	86—90	34.4
3	2 : 1 : 0.3	4.0	71—73	22.3	78—84	20.4
4	3 : 1 : 0.3	4.0	74—80	21.3	80—84	22.5
5	3 : 1 : 0.2	6.5	70—73	32.5	81—85	7.8

Note: Experiment 1 was carried out at 40°, the others at 30°. The reaction time includes the introduction of propylene and the additional stirring of the reaction mass.

TABLE 2. Alkylation of o-Bromophenol by Pentene-2 at Room Temperature

Expt. No.	Molar ratios of bromophenol, pentene-2 and $BF_3 \cdot O(C_2H_5)_2$	Reaction time (hr)	Alkylation products			
			sec-amyl ether of o-bromophenol		4-sec-amyl-o-bromophenol	
			boiling range (pressure in mm)	yield (%)	boiling range (pressure in mm)	yield (%)
1	4 : 1 : 0.2	96	109—130 (3)	30.6	110—126 (5)	17.7
2	4 : 1 : 0.2	48	122—130 (5)	25.9	112—117 (3)	22.7
3*	4 : 1 : 0.2	48	118—130 (7)	5.4	116—119 (5)	4.8
4*	4 : 1 : 0.2**	48	137—147 (10)	22.6	114—118 (5)	17.3
5	3 : 1 : 0.2	48	112—120 (4)	30.4	114—120 (4)	11.5
6	2 : 1 : 0.2	48	114—130 (3)	30.1	114—120 (4)	8.8

* The experiments were carried out in carbon tetrachloride.

** The catalyst was $BF_3 \cdot H_3PO_4$.

Alkylation of o-bromophenol by pentene-1. We placed 69.4 g of o-bromophenol and 8.9 g of $BF_3 \cdot O(C_2H_5)_2$ in a three-necked flask and 14 g of pentene-1 (the molar ratios of the reagents and catalysts were 2 : 1 : 0.3) was added at room temperature with vigorous stirring to the homogeneous transparent light-colored liquid. The reaction mass was then stirred for 10 hr at 14-15°, it was left to stand at this temperature for 61 hr and treated in the usual manner. We separated the sec-amyl ether of 2-bromophenol (III) from the neutral reaction products, with a yield of 20.7 g (42.6%); it distilled at 96-98° (2 mm), $n^{20}D$ was 1.5250. As a result of the distillation of the phenolic products, 8.6 g (17.7%) of 4-sec-amyl-2-bromophenol (IV) was obtained. The product distilled at 90-91° (2 mm), $n^{20}D$ was 1.5400.

We added 7 g of pentene-1 at 40° (molar ratios of the reagent and catalyst 3 : 1 : 0.2) for 1 hr to a dark-brown mixture of 51.9 g of o-bromophenol and 4.1 g of $BF_3 \cdot H_3PO_4$, the reaction mixture was stirred for 2 hr at this temperature and left overnight at room temperature. After the separation of the phenol and ether products, the following were obtained by corresponding treatment: 2.4 g or 9.9% of (III), b.p. 90-91° (2 mm) and 10.1 g or 41.5% of (IV) (b.p. 90-92° at 2 mm, $n^{20}D$ 1.5400). In both experiments the products distilled completely.

Alkylation of o-bromophenol by pentene-2. The reaction was carried out as above. We took 0.1 mole of pentene-2 and corresponding amounts of o-bromophenol and catalyst for each experiment. In experiments with CCl_4 as solvent, o-bromophenol, the catalyst and 120 ml of CCl_4 were placed in the reaction flask, and pentene-2 mixed with 20 ml of CCl_4 was added to the light-colored mixture. During this process the temperature generally rose

spontaneously from 14-15 to 20-23°. After the theoretical amounts of pentene-2 had been added the reaction mass was stirred for 8-10 hr and left for a fixed time at room temperature; the reaction products were then treated in the corresponding manner, separated into the ether and phenolic products and distilled. In the present case, in contrast to the reaction with pentene-1 the ether and phenolic products were distilled in a wide range and 1-3 g of tar always remained in the distillation flask. The results of the experiments are given in Table 2.

Sec-amyl ether of 2-bromophenol (III)—a colorless oily liquid with a pleasant ethereal odor.

B.p. 90-91° (2 mm), d^{20}_4 1.2556, $n^{20}D$ 1.5260, MR_D 59.44; calc. 58.80.

Found %: Br 32.62, 32.72. $C_{11}H_{15}OBr$. Calculated %: Br 32.82.

Simple sec-amyl ether of salicylic acid; this was obtained by substitution of bromine in (III) by a carboxyl group via organomagnesium synthesis, with a yield of 73.7%. It is a colorless liquid.

B.p. 150-151° (2 mm), d^{20}_4 1.0872, $n^{20}D$ 1.5200, MR_D 58.22; calc. 57.19.

Found: M 208.4, 208.4. $C_{12}H_{16}O_{13}$. Calculated: M 208.2.

4-Sec-amyl-2-bromophenol (IV) is a colorless oily liquid with a slight phenolic odor.

B.p. 84-85° (1 mm), d^{20}_4 1.2843, $n^{20}D$ 1.5427, MR_D 58.70; calc. 59.58.

Found %: Br 32.73. $C_{11}H_{15}OBr$. Calculated %: Br 32.82.

Methyl ether of 4-sec-amyl-2-bromophenol; this was obtained by methylation of (IV) with methyl iodide. It is a colorless liquid with a pleasant odor. Its constants correspond to the product obtained by the alkylation of o-bromoanisole by pentene-1.

B.p. 107-109° (1 mm), d_4^{20} 1.2458, n_D^{20} 1.5323, MR_D 63.98; calc. 63.42.

SUMMARY

The reaction of o-bromophenol with propylene, pentene-1 and pentene-2 in the presence of the catalysts $BF_3 \cdot O(C_2H_5)_2$ and $BF_3 \cdot H_3PO_4$ was investigated. It is shown that alkyl ethers of o-bromophenol and 4-alkyl-2-bromophenols are formed with all olefins. Their total yield and relative amounts depend on temperature, the amounts and nature of the catalyst.

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CYCLOPROPANES AND CYCLOBUTANES

XVI.* p-CHLORO AND p-BROMOPHENYLCYCLOBUTANES

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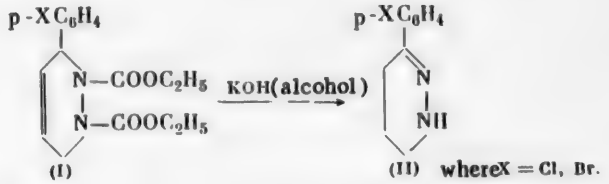
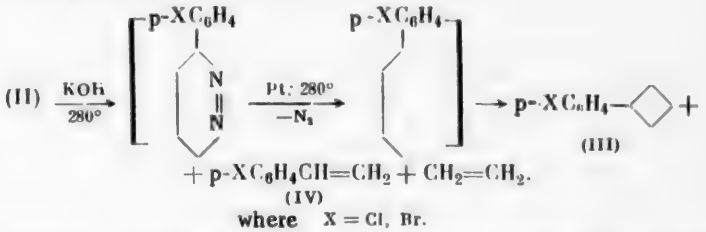
The investigation of the catalytic decomposition of 3-aryl tetrahydropyridazines (by heating in the presence of caustic potash and platinum) led us to the development of a method of synthesizing aryl cyclobutanes [1-3]. In the present work this reaction was extended to 3-p-chlorophenyl- and 3-p-bromophenyltetrahydropyridazines. Both tetrahydropyridazines (II) were obtained by hydrolysis of the corresponding 1,2-dicarbethoxy-3-aryl-tetrahydropyridazines (I) [3, 4].



(I) (II) where X = Cl, Br.

The tetrahydropyridazines (II) were subjected to catalytic decomposition (in the presence of caustic potash and platinum). It was found that in this case, decomposition takes place in the expected way [1-3]: the reaction products are the corresponding aryl cyclobutanes (III) and styrenes (IV).



where X = Cl, Br.

The ratio of the amounts of aryl cyclobutane and styrene was appreciably different in both cases. For p-chlorophenyltetrahydropyridazine it was 0.8, i.e., of the same order as in the case of tolyl- and anisyltetrahydropyridazines [3], while for p-bromophenyltetrahydropyridazine it was much greater, i.e., 3.5. After treatment with 2,4-dinitrophenylsulfenyl chloride [5] the aryl cyclobutanes obtained did not contain an admixture of unsaturated compounds (according to the combined dispersion spectra). Figures 1 and 2 show the ultraviolet absorption spectra of the corresponding aryl cyclopropanes; for purposes of comparison the same figures give the ultraviolet absorption spectra of the corresponding aryl cyclopropanes. From these figures it is seen that the aryl cyclobutanes we investigated have mainly a characteristic absorption minimum in the wavelength region of 240-245 mμ, and a characteristic maximum in the 260-270 mμ region, as in the case of the aryl cyclobutanes, which we previously investigated [3]. The ultraviolet absorption spectra of aryl cyclobutanes and the corresponding aryl cyclopropanes have a similar character.

* For communication XV see Doklady Akad. Nauk SSSR 135, 879 (1960).

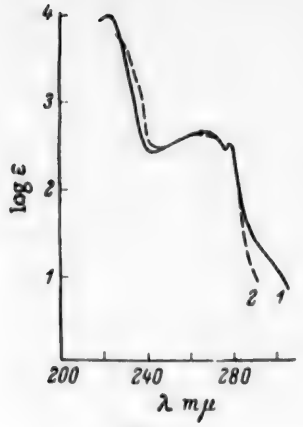


Fig. 1

1) p-Chlorophenylcyclobutane. λ_{max} 224 mμ, $\log\varepsilon_{max}$ 4.07; λ_{min} 241 mμ, $\log\varepsilon_{min}$ 2.43; λ_{max} 270 mμ, $\log\varepsilon_{max}$ 2.72; λ_{min} 278 mμ, $\log\varepsilon_{min}$ 2.45; λ_{max} 277 mμ, $\log\varepsilon_{max}$ 2.66;
2) p-Chlorophenylcyclopropane. λ_{min} 248 mμ, $\log\varepsilon_{min}$ 2.48; λ_{max} 265 mμ, $\log\varepsilon_{max}$ 2.62; λ_{min} 270 mμ, $\log\varepsilon_{min}$ 2.59; λ_{max} 272 mμ, $\log\varepsilon_{max}$ 2.62; λ_{min} 278 mμ, $\log\varepsilon_{min}$ 2.42; λ_{max} 280 mμ, $\log\varepsilon_{max}$ 2.51.

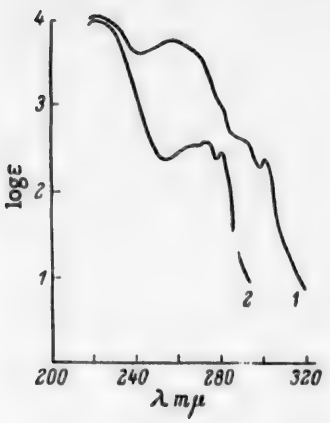
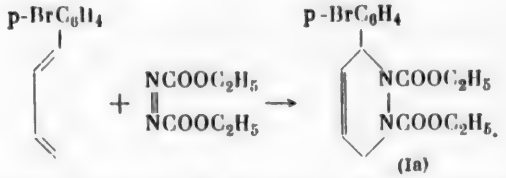


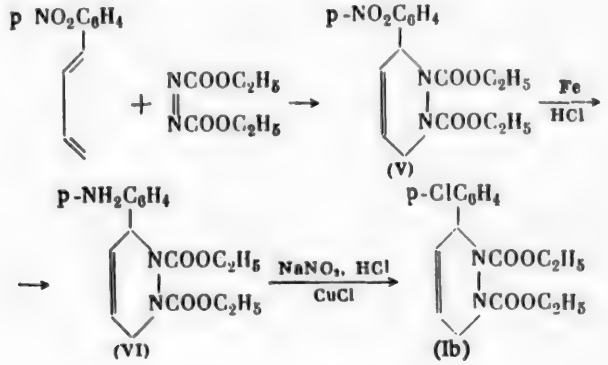
Fig. 2

1) p-Bromophenylcyclobutane. λ_{max} 222 mμ, $\log\varepsilon_{max}$ 4.04; λ_{min} 243 mμ, $\log\varepsilon_{min}$ 3.62; λ_{max} 258 mμ; $\log\varepsilon_{max}$ 3.75; λ_{min} 298 mμ, $\log\varepsilon_{min}$ 2.31; λ_{max} 300 mμ, $\log\varepsilon_{max}$ 2.38;
2) p-bromophenylcyclopropane. λ_{max} 223 mμ, $\log\varepsilon_{max}$ 3.91; λ_{min} 252 mμ, $\log\varepsilon_{min}$ 2.35; λ_{max} 266 mμ, $\log\varepsilon_{max}$ 2.52; λ_{min} 270 mμ, $\log\varepsilon_{min}$ 2.51; λ_{max} 273 mμ, $\log\varepsilon_{max}$ 2.56; λ_{min} 278 mμ, $\log\varepsilon_{min}$ 2.36; λ_{max} 280 mμ, $\log\varepsilon_{max}$ 2.43.

The initial dicarbethoxytetrahydropyridazines of structure (I) were synthesized in two ways: 1,2-dicarbethoxy-3-p-bromophenyltetrahydropyridazine (Ia) was obtained in the ordinary way—by the reaction of azodicarboxylic ester with 1-(p-bromophenyl)-butadiene (the latter was obtained by halogenation diarylation of divinyl [6].



An essentially different method was selected for obtaining 1,2-dicarbethoxy-3-p-chlorophenyltetrahydropyridazine (Ib): preparation of the addition product (V) of p-nitrophenylbutadiene* with azodicarboxylic ester and its conversion according to the following system:



*p-Nitrophenylbutadiene is one of the most readily available arylbutadienes: it is obtained easily and with a high yield by dehydrochlorination of 4-chloro-1-p-nitrophenylbutene-2, the reaction product of p-nitrophenyl diazonium chloride and divinyl [7].

The reaction of nitrophenylbutadiene with azodicarboxylic ester is not described in the literature. Like 1,2-dicarbethoxy-3-p-nitrophenyltetrahydropyridazine (V), the structure of this reaction product was proven by conversion of the amine (VI) obtained from it, to the previously described [1, 8] 1,2-dicarbethoxy-3-phenyltetrahydropyridazine (VII).

It was not expedient to obtain 1,2-dicarbethoxy-3-p-bromophenyltetrahydropyridazine (Ia) on the basis of this addition product because in the stage of substitution of the amino group by bromine its subsequent elimination took place and a very difficulty separable mixture of tetrahydropyridazines (Ia and VII) was formed.

EXPERIMENTAL

1-p-Nitrophenylbutadiene-1,3 was obtained by condensation of p-nitrophenyl diazonium chloride with divinyl in the presence of cupric chloride, followed by dehydrochlorination of the 4-chloro-1-p-nitrophenylbutene-2. by the method in [7]. The yield was 70%; the m.p. was 77-78° (from ligroin). According to [7] the m.p. is 78-78.8°.

1-p-Bromophenylbutadiene-1,3* was obtained in a similar way to [6]. The yield was 15-20%, the b.p. was 124-125° (10 mm); the m.p. was 27-28°. According to [7], the b.p. is 110° (3 mm) and the m.p. 29°.

Addition products of aryl butadienes and azodicarboxylic ester. 1,2-Dicarbethoxy-3-p-bromophenyl-1,2,3,6-tetrahydropyridazine (Ia) was obtained (85-87% yield) by mixing equimolecular amounts of diene and azodicarboxylic ester in absolute ether. After the ether had been driven off, the residue was distilled under vacuum.

B.p. 198-199° (3 mm), $n^{20}D$ 1.5348, d^{20}_4 1.3499, MR_D 88.77. $C_{16}H_{19}O_4N_2BrF_4$. Calculated 88.36.**

Found %: N 7.79, 7.84. $C_{16}H_{19}O_4N_2Br$. Calculated %: N 7.31.

1,2-Dicarbethoxy-3-p-nitrophenyl-1,2,3,6-tetrahydropyridazine (V). A solution of equimolecular amounts of the reagents in anhydrous benzene was heated for 1 hr; after the solvent had been distilled off, the mass which crystallized on standing was filtered at the pump, washed with ligroin and recrystallized from the latter. The yield was 90-95%, the m.p. was 84.84.5°.

Found %: C 55.08, 55.11; H 5.52, 5.46; N 11.78, 11.70. $C_{16}H_{19}O_6N_3$. Calculated %: C 55.01; H 5.48; N 12.03.

1,2-Dicarbethoxy-3-p-aminophenyl-1,2,3,6-tetrahydropyridazine (VI). A solution of 34.8 g (0.1 mole) of the nitro compound (V) in 50 ml of alcohol and 16.8 g (0.3 g-at) of reduced iron powder were placed in a three-necked flask. After 70 ml (0.8 mole) of concentrated hydrochloric acid had been added for 1 hr with vigorous stirring and heating, the mixture was heated for a further 15-20 min and the viscous reddish brown liquid was neutralized. The dark-green precipitate obtained, which turned slightly brown in air, was filtered at the pump and extracted with ether in a Soxhlet. When the ether had been removed the amine (VI) crystallized in the form of light-yellow needles. The yield was 28.7 g (90%); the m.p. was 85-86° (from ligroin).

Found %: C 60.45, 60.49; H 6.84, 6.66; N 13.11, 13.10. $C_{16}H_{21}O_4N_3$. Calculated %: C 60.18; H 6.63; N 13.16.

Elimination of the amino group in the amine obtained [proof of the structure of amine (VI) and therefore the nitro compound (V)]. We dissolved 3.67 g (0.012 mole) of the amine in 2.7 ml of concentrated hydrochloric acid and 9 ml of water and diazotized it at −5°−−2° with 0.84 g (0.012 mole) of sodium nitrite in 5 ml of water. The diazo solution was added slowly and with stirring to a cooled (0°) solution of 0.56 g (0.006 mole) of paraform in 12 ml of 4 N solution of caustic soda; when all the solution had been added the mixture was stirred for a further 10 min. The reaction product was extracted with ether, washed with water and dried with calcium chloride. The ether was driven off and the residue was distilled under vacuum, the 195-200° (10 mm) fraction being selected; the latter crystallized out on standing. After recrystallization from ligroin the substance obtained melted at 47°. A mixed sample of this compound with 1,2-dicarbethoxy-3-phenyl-1,2,3,6-tetrahydropyridazine (m.p. 47°) obtained by diene synthesis from 1-phenylbutadiene-1,3- and azodicarboxylic ester [1] showed no depression of the melting point.

* Attempts to synthesize bromophenylbutadiene by dehydration of the carbinol obtained by organomagnesium synthesis from p-bromobenzaldehyde and allyl chloride were unsuccessful (intense tarring).

** The atomic refraction of nitrogen was taken as 2.48 [10].

1,2-Dicarbethoxy-3-p-chlorophenyl-1,2,3,6-tetrahydropyridazine (Ib). We diazotized 38.8 g (0.1 mole) of the amine (VI) by the usual method. The solution of the diazo compound was added in small portions to a well stirred and cooled (−5°) mixture of 60 ml of acetone and 16 g (0.08 mole) of cuprous chloride. When vigorous frothing of the mixture had ceased, it was gradually brought to room temperature; the reaction mixture was then heated at 40-50° until liberation of nitrogen had ceased, and was extracted with ether and dried with calcium chloride. The solvent was distilled and the residue was fractionated under vacuum. The yield was 21.3 g (63%).

B.p. 175-176° (4 mm), $n^{20}D$ 1.5268, d^{20}_4 1.2122, MR_D 85.12. $C_{16}H_{19}O_4N_2ClF_4$. Calculated 85.32.

Found %: N 8.04, 7.99. $C_{16}H_{19}O_4N_2Cl$. Calculated %: N 8.27.

3-Aryl-1,4,5,6-tetrahydropyridazine (II) was obtained by hydrolysis and decarboxylation of the dicarbethoxy compounds (Ia and Ib) by the usual method [3].

3-p-Chlorophenyl-1,4,5,6-tetrahydropyridazine (yield 46%, m.p. 61-62°). The addition product with phenylisothiocyanate (the anilide of 3-p-chlorophenyl-1,4,5,6-tetrahydropyridazine-1-thiocarboxylic acid) melted at 143° (from alcohol).

Found %: N 12.52, 12.58. $C_{17}H_{16}N_3SCl$. Calculated %: N 12.74.

3-p-Bromophenyl-1,4,5,6-tetrahydropyridazine (yield 44%); m.p. 52-53°. The addition product with phenylisothiocyanate; m.p. 147.5-148° (from alcohol).

Found %: C 54.65, 54.77; H 4.44, 4.23; N 10.98, 10.90. $C_{17}H_{16}N_3SBr$. Calculated %: C 54.53; 4.31; N 11.23.

Aryl cyclobutanes were obtained by catalytic decomposition of 3-aryl tetrahydropyridazines by the method we described in [1-3].

3-p-Chlorophenylcyclobutane was obtained by decomposition of 3-p-chlorophenyl-1,4,5,6-tetrahydropyridazine; the yield was 23%. After the removal of traces of p-chlorostyrene by 2,4-dinitrophenylsulfenyl chloride [5] it had the following constants:

B.p. 103.5-104.5° (10 mm), $n^{20}D$ 1.5375, d^{20}_4 1.1122. MR_D 47.79. $C_{10}H_{11}ClF_3\square$. Calculated 47.88.

Found %: C 71.90, 72.07; H 6.63, 6.80. $C_{10}H_{11}Cl$. Calculated %: C 72.07; H 6.65.

The by-product of the reaction, p-chlorostyrene (yield 32%), was also obtained.

B.p. 69-70° (10 mm), $n^{20}D$ 1.5735, d^{20}_4 1.15.47. According to [9]: b.p. 33-38° (0.4 mm), $n^{20}D$ 1.5742, d^{20}_4 1.1554.

Analysis of the gas liberated during decomposition showed that it consisted of 64% nitrogen and 36% of unsaturated hydrocarbons.

3-p-Bromophenylcyclobutane (obtained by decomposition of 3-p-bromophenyl-1,4,5,6-tetrahydropyridazine; yield 16%).

B.p. 107-108° (10 mm), $n^{20}D$ 1.5643, d^{20}_4 1.3435, MR_D 51.10. $C_{10}H_{11}BrF_3\square$. Calculated 50.83.

Found %: C 56.75, 56.50; H 5.08, 5.11. $C_{10}H_{11}Br$. Calculated %: C 56.89; H 5.26.

p-Bromostyrene (yield 4.5%)

B.p. 86-88° (10 mm), $n^{20}D$ 1.5929, d^{20}_4 1.3993. According to [9]: b.p. 78° (13 mm), $n^{20}D$ 1.5933, d^{20}_4 1.400. The gas consisted of 82% of nitrogen and 18% of unsaturated hydrocarbons.

SUMMARY

1. It was shown that our previously developed method for the synthesis of aryl cyclobutanes—catalytic decomposition of 3-aryl tetrahydropyridazines—can also be used for obtaining cyclobutanes containing halogen in the aromatic ring.

2. It was established that p-nitrophenyl- and p-bromophenylbutadienes react with azodicarboxylic ester by the system of diene synthesis.

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AROMATIC HYDROCARBONS

XVII. THE SYNTHESIS OF PHENANTHRENES

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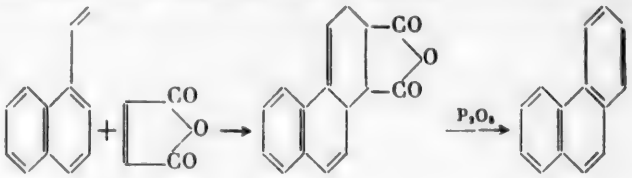
Original article submitted March 21, 1960

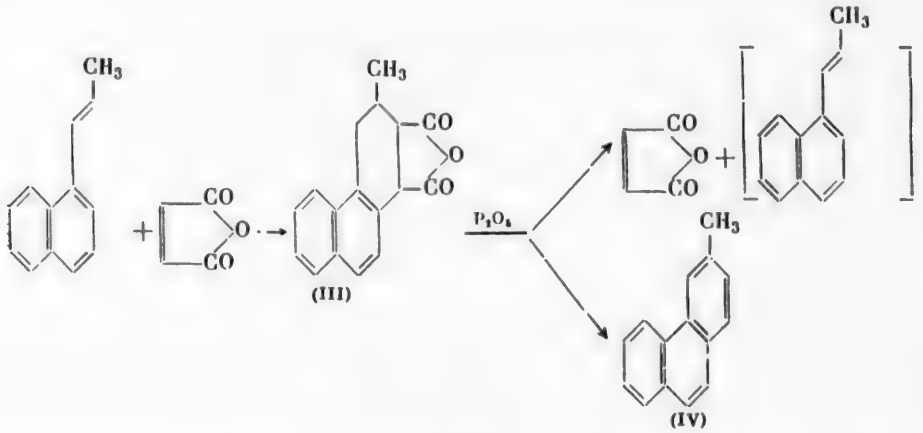
The aromatization reaction under the influence of phosphorus pentoxide on adducts of diene hydrocarbons with maleic anhydride, its homologs, and cyclic analogs [1] has been used in the present work for the preparation of hydrocarbons of the phenanthrene series. As the starting diene components for preparing phenanthrene, 1-methyl-, 3-methyl-, and 1,3-dimethylphenanthrenes we have used α-vinyl and α-propenylnaphthalenes.

Phenanthrene (II) was obtained with a yield of 27% by the action of phosphorus pentoxide on the adduct of α-vinylnaphthalene with maleic anhydride, the anhydride of 1,2,3,11-tetrahydrophenanthrene-1,2-dicarboxylic acid (I).



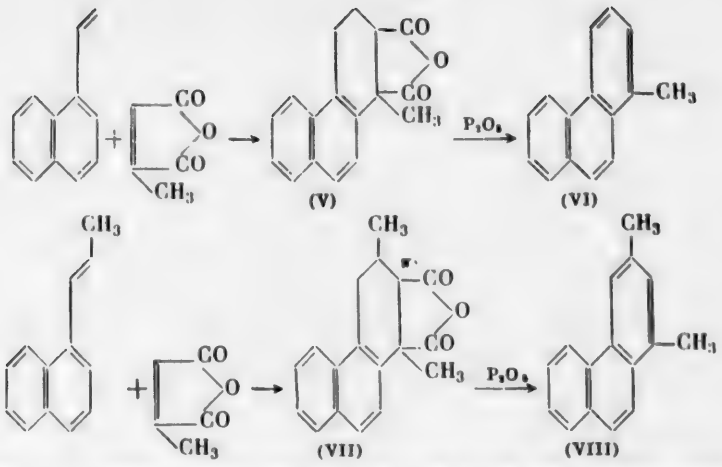
(I) (II)

For the preparation of 3-methylphenanthrene (IV) we heated the adduct of α-propenylnaphthalene and maleic anhydride, the anhydride of 3-methyl-1,2,3,4-tetrahydrophenanthrene-1,2-dicarboxylic acid (III), with phosphorus pentoxide. However, it was shown that under these conditions anhydride (III) undergoes preferentially a retrodiene splitting; from the reaction products we isolated maleic anhydride, and the α-propenylnapthalene which formed was completely converted to tar. Only a small amount of the starting anhydride (III) aromatized with splitting out of carbon monoxide and water to give 3-methylphenanthrene (IV) which was identified by melting point and melting of its picrate.



(III) (IV)

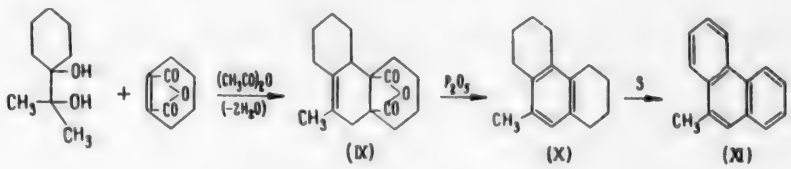
1-Methylphenanthrene (VI) and 1,3-dimethylphenanthrene (VIII) were obtained with 40% yields by aromatization under the influence of phosphorus pentoxide on the adducts (V) and (VII) of α-vinylnaphthalene and α-propenylnaphthalene respectively with methyl maleic anhydride.



The resulting methylphenanthrenes were identified by melting points and melting points of the picrates. For identification of 1,3-dimethylphenanthrene we also studied its ultraviolet absorption spectrum, which agreed with the spectrum of 1,3-dimethylphenanthrene as given in the literature [2].

The preparation only of 1-methylphenanthrene from adduct (V) and 1,3-dimethylphenanthrene from adduct (VII) without admixtures of their isomeric hydrocarbons with other positions for the methyl group is evidence of the structure of the adducts of α-vinyl- and α-propenylnaphthalenes with such unsymmetrical dienophils as methylmaleic anhydride.

For the preparation of 9-methylphenanthrene (XI) one of the intermediate stages of the synthesis is also the action of phosphorus pentoxide on the adduct of the diene synthesis (IX). In this synthesis the dienophil component is tetrahydrophthalic anhydride, and the diene component the mixed pinacone* from acetone and cyclohexanone, formed in the process of the diene synthesis of isopropenylcyclohexene.



EXPERIMENTAL

α-Vinylnaphthalene was obtained with 80% yield from 2-(α-naphthyl)-ethanol (m.p. 60°) by leading its benzene solution over aluminum oxide at 345-350° in a stream of nitrogen.

B.p. 123-124° (12 mm), $n^{20}D$ 1.6385; literature values [4]: b.p. 105-106° (6 mm), $n^{20}D$ 1.6388.

α-Propenylnaphthalene was obtained in 74% yield under the same conditions by dehydration of α-naphthylethyl carbinol (m.p. 64°) at 310-320°.

B.p. 144-145° (11 mm), $n^{20}D$ 1.6310; literature values [5]: b.p. 143-144° (11 mm), $n^{20}D$ 1.6315.

The anhydride of 1,2,3,11-tetrahydrophenanthrene-1,2-dicarboxylic acid (I) was obtained by 20 min heating in benzene solution of equimolecular amounts of α-vinylnaphthalene with maleic anhydride and later standing for three days at room temperature; m.p. 184-186° (from acetic anhydride); yield 35%.

Literature value [6]: m.p. 187.5-190°.

* The diene synthesis with pinacones instead of diene hydrocarbons obtained from them was previously described by us [3].

The anhydride of 3-methyl-1,2,3,4-tetrahydrophenanthrene-1,2-dicarboxylic acid (III) was obtained by six hour heating on a boiling water bath of a mixture of 10 g of α-propenylnaphthalene and 24 g of maleic anhydride. On the next day, adduct (III) (9.9 g, yield 62%) was washed with ether and recrystallized from acetic acid; m.p. 268-270°.

Literature value [7]: m.p. 271.8°.

Anhydride of 1-methyl-1,2,3,4-tetrahydrophenanthrene-1,2-dicarboxylic acid (V) was obtained by 17 hr heating of 24 g of α-vinylnaphthalene and 52 g of methylmaleic anhydride in 130 ml of propionic acid. After distillation of the propionic acid and excess methylmaleic anhydride the residue was distilled in a vacuum. We isolated 14.5 g (35%) of adduct (V) with b.p. 220-235° (5 mm), m.p. 142.3-142.7° (three crystallizations from a mixture of benzene and ligroin).

Literature value [6]: m.p. 140.8-141.1°.

Found %: C 76.57, 76.74; H 5.34, 5.33. $C_{17}H_{14}O_3$. Calculated %: C 76.67; H 5.30.

The acid obtained from adduct (V) melted at 215-220° (from acetic acid).

The anhydride of 1,3-dimethyl-1,2,3,4-tetrahydrophenanthrene-1,2-dicarboxylic acid (VII) was obtained by 17 hr heating in a stream of nitrogen of 21 g of α-propenylnaphthalene and 14 g of methylmaleic anhydride in 15 ml of acetic acid. Distillation of the reaction mixture in a vacuum gave adduct (VII) (5.6 g, yield 16%) with b.p. 220-230° (2 mm), m.p. 195-195.5° (from acetic acid).

Found %: C 77.22, 77.44; H 6.06; 5.78. $C_{18}H_{16}O_3$. Calculated %: C 77.11; H 5.75.

Adduct of isopropenyl-1-cyclohexene with Δ'-tetrahydrophthalic anhydride (anhydride of 9-methyl-$\Delta^{9,14}$-dodecahydrophenanthrene-11,12-dicarboxylic acid) (IX). The preparation of adduct (IX) was carried out by heating 20 g of mixed pinacone (m.p. 80-82°, from acetone and cyclohexanone) with 48.7 g of Δ'-tetrahydrophthalic anhydride (m.p. 69-70°) in 200 ml of acetic anhydride; distillation of the reaction mixture in a vacuum gave adduct (IX) (7.2 g, yield 20%) with b.p. 190-200° (7-8 mm), m.p. 155-156° (from a mixture of benzene and ligroin).

Found %: C 74.04, 74.00; H 8.09, 7.97. $C_{17}H_{22}O_3$. Calculated %: C 74.42; H 8.08.

Phenanthrene (II). Adduct (I) (9 g) was gradually heated in a Wurtz flask on a metal bath with 5 g of phosphorus pentoxide. The resulting hydrocarbon (1.7 g, yield 27%) distilled at once from the reaction mixture by heating in a vacuum of 5-10 mm and was purified by chromatography from a benzene solution on aluminum oxide; m.p. 99° (after three crystallizations from alcohol). Picrate m.p. 144°.

A sample mixed with known phenanthrene and a sample mixed with the picrate gave no melting point depression.

Literature values [8]: phenanthrene m.p. 100°, picrate m.p. 145°.

3-Methylphenanthrene (IV). We heated 4.7 g of adduct (III) and 2.5 g of phosphorus pentoxide in a Wurtz flask for 1.5 hr from 280 to 370° until evolution of carbon monoxide stopped; the maleic anhydride which formed distilled out in a vacuum (b.p. 250-255° at 15 mm; m.p. 52.5°, no depression with known maleic anhydride) and the residue was extracted with hot alcohol. The alcoholic solution of hydrocarbon (IV) obtained thus was purified by passing through a column filled with aluminum oxide; the alcohol was partly distilled off and by the addition of picric acid after long standing there was isolated the picrate with m.p. 137-138°. 3-Methylphenanthrene was obtained by decomposition of the picrate by heating with ammonia, and after crystallization from alcohol melted at 61-62°.

Literature value [9]: m.p. 62-63°.

Picrate m.p. 139-140.5°.

1-Methylphenanthrene (VI). Eight g of adduct (V) and 4 g of phosphorus pentoxide were gradually heated on a metal bath from 230 to 350° and the hydrocarbon which formed was distilled off in a vacuum, yield 2.2 g (40%), m.p. 116-117° (after three crystallizations from alcohol); picrate m.p. 135-136°.

Literature values [6]: 1-methylphenanthrene m.p. 116-118°, picrate m.p. 135.7-136.2°; 2-methylphenanthrene, m.p. 55-56°, picrate m.p. 118-119°.

1,3-Dimethylphenanthrene (VIII) was obtained by the same method as 1-methylphenanthrene from 5 g of adduct (VII); yield 1.3 g (40%), m.p. 74.5-75.7° (from alcohol); picrate m.p. 155-155.6°.

Literature values: 1,3-dimethylphenanthrene m.p. 75-76°, picrate m.p. 154-155° [10]; 2,3-dimethylphenanthrene m.p. 79-80°, picrate m.p. 145-146° [9].

9-Methylphenanthrene (XI). Gradual heating of 13.7 g of adduct (IX) and 7.5 g of phosphorus pentoxide until evolution of carbon monoxide stopped and later distillation of the reaction mixture in a vacuum gave 9-methyl-1,2,3,4,5,6,7,8-octahydrophenanthrene (X), yield 7 g (70%).

B.p. 182-183° (13 mm), $n^{20}D$ 1.5668, d^{20}_4 1.020, MR_D 64.13. $C_{15}H_{20}F_3$. Calculated 63.47.

Literature values [10]: b.p. 145-146° (3 mm), $n^{20}D$ 1.5640, d^{20}_4 1.0171.

By heating 9-methyloctahydrophenanthrene (X) with sulfur at 230-250° it was converted into hydrocarbon (XI) which was purified by sublimation and after two recrystallizations from alcohol melted at 89-90°; picrate m.p. 152-153°.

Literature values [10]: m.p. 88-89°, picrate m.p. 151-153°.

SUMMARY

For preparing phenanthrene and its close homologs, 1-methyl-, 3-methyl-, 9-methyl-, and 1,3-dimethylphenanthrenes we have used the reaction of tetrahydrophthalic anhydrides (adducts of the diene synthesis) with phosphorus pentoxide.

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THE SYNTHESIS OF ARYLAMIDES OF CYCLOPENTANON-2-CARBOXYLIC ACID

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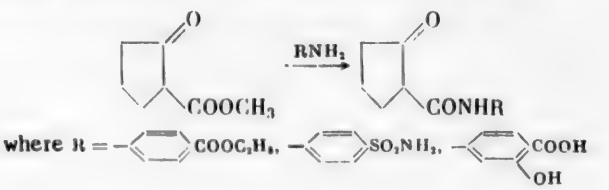
Original article submitted March 26, 1960

According to the literature, ethyl cyclopentanon-2-carboxylate at room temperature reacts with primary aromatic amines with formation of esters of 2-arylamino-$\Delta^{1,2}$-cyclopentene carboxylic acid [1]. At higher temperature the reaction is accompanied by splitting out of a molecule of alcohol which leads to formation of an arylamide of cyclopentanon-2-carboxylic acid [2]. Considering the wide use of carboxylic acid amides as medicinal agents and also the expanding use of cyclopentanone carboxylic esters for preparing pharmacologically active substances [3], we have synthesized some amides of cyclopentanon-2-carboxylic acid in order to study further their biological activity.

Methyl cyclopentanon-2-carboxylate was obtained by cyclization of dimethyl adipate. As the starting aromatic amines we used anesthesine, sulfanilamide, and p-aminosalicylic acid.



The reaction was carried out by heating methyl cyclopentanon-2-carboxylate and the substituted aromatic amines without a solvent. The temperature of the reaction mass and the duration of the reaction depended on the initiation and duration of splitting out of methyl alcohol, controlled by evolution of bubbles of vapor. The condensation products were white or slightly colored crystalline substances, insoluble in water and acids, slightly soluble in cold alcohol, easily soluble in boiling alcohol. The presence of a ketone group was shown by the formation of a 2,4-dinitrophenylhydrazone [4]. It whould be mentioned that the derivative of anesthesine easily forms a 2,4-dinitrophenylhydrazone at room temperature while for the preparation of the 2,4-dinitrophenylhydrazone of the sulfanilamide derivative boiling is required. The 2,4-dinitrophenylhydrazone of the condensation product from p-aminosalicylic acid and the cyclopentanone carboxylate is difficult to purify and on analysis does not give satisfactory results, and so the amide was converted by the action of a copper sulfate solution to the copper salt and was analyzed gravimetrically.

EXPERIMENTAL

p-Carbethoxyphenyl amide of cyclopentanon-2-carboxylic acid. We heated 17 g of methyl cyclopentanon-2-carboxylate and 19.8 g of anesthesine for 20 min at 128-130°; on the next day the precipitate was filtered off, washed with alcohol, and recrystallized from alcohol. We obtained 7.1 g (21.0%) of a white, crystalline powder, m.p. 143-144°.

Found %: N 5.18, 5.26. $C_{15}H_{17}O_4N$. Calculated %: N 5.09.

2,4-Dinitrophenylhydrazone consisted of fine yellow crystals, m.p. 211-212.5° (from dichloroethane).

Found %: N 15.75, 15.57. $C_{21}H_{21}O_7N_5$. Calculated %: N 15.33.

p-Carboxy-m-hydroxyphenylamide of cyclopentanon-2-carboxylic acid. Fifteen g of methyl cyclopentanon-2-carboxylate and 10.8 g of p-aminosalicylic acid were heated for 7 min at 118°. After recrystallization from butanol we obtained white crystals with a yellow tint, m.p. 202° (decomposition); yield 17.1 g (92.3%).

Found %: N 4.85, 5.09. $C_{13}H_{13}O_5N$. Calculated %: N 5.32.

For preparation of the 2,4-dinitrophenylhydrazone we added to a boiling solution of the substance in butyl alcohol a solution of 2,4-dinitrophenylhydrazine in alcohol which contained sulfuric acid. The mixture was boiled for one hour. The resulting cherry red crystals did not melt up to 270°. The copper salt was obtained by solution of the condensation product in 0.1 N sodium hydroxide solution followed by addition of a 5% copper sulfate solution. The light green precipitate was filtered off, washed with water, and dried.

Found %: Cu 10.65, 10.42. $C_{26}H_{24}O_{10}N_2Cu$. Calculated %: Cu 10.80.

p-Sulfamidophenylamide of cyclopentanone-2-carboxylic acid. We heated 7.8 g of sulfanilamide and 9.7 g of methyl cyclopentanone-2-carboxylate for ten minutes at 130-142°. After repeated recrystallizations from alcohol (with charcoal) we obtained a white, crystalline powder with a lilac tint, m.p. 212° (decomposition), yield 9.22 g (72.1%).

Found %: N 10.04, 10.01; S 11.11, 11.05. $C_{12}H_{14}O_4N_2S$. Calculated %: N 9.99; S 11.35.

2,4-Dinitrophenyl hydrazone was obtained by boiling an alcoholic solution of the substance with an alcoholic solution of 2,4-dinitrophenylhydrazine which contained sulfuric acid. After recrystallization from alcohol we obtained yellow crystals, m.p. 218° (decomposition).

Found %: N 17.83, 18.06. $C_{18}H_{18}O_7N_6S$. Calculated %: N 18.18.

SUMMARY

We have shown that methyl cyclopentanone-2-carboxylate heated with anesthesine, p-aminosalicylic acid, or sulfanilamide forms the corresponding amide of cyclopentanone-2-carboxylic acid, characterized through the 2,4-dinitrophenylhydrazone (or copper salt).

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ADDITION REACTIONS OF ACETYLENE CARBOXYLIC ACIDS AND THEIR ESTERS

I. THE REACTION OF ACETYLENE DICARBOXYLIC ACID AND ITS ESTERS WITH ARYLSULFINIC ACIDS

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Acetylene dicarboxylic acid (ADA) and its esters resemble benzoquinone in many addition reactions. This is evidently connected with the presence in these substances of a related system of atoms which consists of two carbonyls joined by a multiple bond.

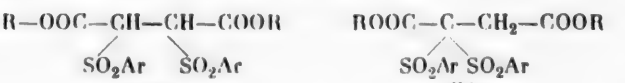
Thus, like quinone, [1], ADA and its esters add alcohols and phenols [2], thiols [3], amines [4], and also enter the diene synthesis [5].

One of the characteristic reactions of benzoquinone is the addition of arylsulfinic acids [6]. So far as we know, a similar reaction for ADA has not been described in the literature.*

It is of interest to determine to what extent this analogy in the reactions of quinone and ADA applies to the reaction with arylsulfinic acids. Also, the sulfones expected as a result of the reaction may be of interest in the investigation of antibacterial activity.**

We have carried out the reaction of ADA and its methyl and ethyl esters with benzenesulfinic, p-toluenesulfinic, and p-nitrobenzenesulfinic acids. ADA was obtained from dibromosuccinic acid [9] and the electrochemical oxidation of butyne diol [10]. The reaction of acetylene dicarboxylic acid with arylsulfinic acids was carried out in glacial acetic acid. In distinction from the free acid the esters of ADA do not react with arylsulfinic acids in glacial acetic acid, but the reaction takes place in a completely satisfactory manner by heating the mixture in methanol. As a result of the reaction we obtained colorless, crystalline sulfones which, to judge by the analyses, were products of the addition of two molecules of sulfinic acid to acetylene dicarboxylic acid and its esters.

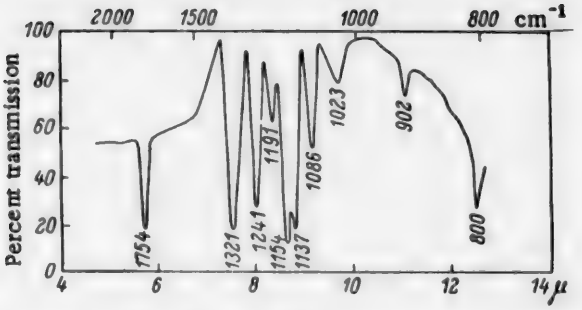
The addition of arylsulfinic acids is possible in two directions



The literature mentions both cases of addition for the analogous reaction of ADA and its esters with thiols. Thus, thioacetic acid forms with acetylene dicarboxylic acid and its dimethyl ester α,α'-di(acetylthio)-succinic acid and its dimethyl ester [11], that is, compounds of type (a); the methylester of thioglycolic acid gives with dimethyl acetylene dicarboxylate the dimethyl ester of α,α'-di(carbomethoxymethylthio)-succinic acid [12], a compound of type (b).

* Only the analogous reaction is known, of addition of p-toluenesulfinic acid to α,β-acetylene ketones [7]. As a result of this reaction there was obtained an unsaturated sulfone of the structure $R-C(SO_2Ar) = CH-COR'$.

** There are descriptions in the literature of α,β-unsaturated sulfones obtained by oxidizing the corresponding sulfides. These compounds were synthesized for a study of antibacterial activity [8].

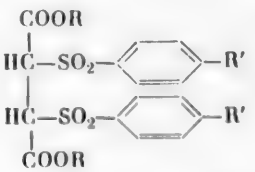


Infrared absorption spectrum of α,α'- di(phenylsulfonyl)-succinic acid (I).

The addition products of arylsulfinic acids to esters of acetylene dicarboxylic acid which we have obtained react with sodium with evolution of hydrogen, which shows the presence of the CH-group between the two electro-
negative residues: $-OC-\underset{|}{CH}-SO_2$. When heated with dilute solutions of potassium hydroxide the sulfones are smoothly hydrolyzed with splitting out of sulfinic acids. From the acidified hydrolyzates the sulfinic acids were isolated as adducts with benzoquinone.

In the infrared spectra of the addition products we observed strong absorption bands in the regions 1335-1320 and 1154-1130 cm^{-1} which are characteristic for asymmetrical and symmetrical oscillation of the SO_2 group [13]. Carboxylic acid (ester) residues are shown by the presence of strong absorption bands in the region 1740-1716 cm^{-1} [14]. Along with this, in the spectra of addition products of benzene sulfinic acid to ADA (a compound which does not contain methyl groups) there is no absorption band in the region 1470-1405 cm^{-1}, which is due to shearing oscillation of the CH_2 group [13] (figure).

The data of the infrared spectra and the chemical behavior of the substances (splitting out arylsulfinic acid in hydrolysis, presence of "acid" hydrogen in the esters of the disulfones) permits the suggestion that in this case there is formation of symmetrical • addition products (I-VII) (table).



(I) R = H, R' = H;
(II) R = CH_3, R' = H;
(III) R = C_2H_5, R' = H;
(IV) R = H, R' = CH_3;
(V) R = CH_3, R' = CH_3;
(VI) R = C_2H_5, R' = CH_3;
(VII) R = H, R' = NO_2.

EXPERIMENTAL

Acetylene dicarboxylic acid, m.p. 174-176° (decomposition), (176-177° with decomposition [9]) was obtained from α, β-dibromosuccinic acid. For the esterification we took acetylene dicarboxylic acid obtained by electrochemical oxidation of butynediol, m.p. 167-172° (decomposition). The method described in the literature [10] was somewhat simplified by us: as the anode we used a lead coil (working surface 1 cm^2) which was placed in a 750 ml porous ceramic vessel set within a thick walled 1.5 liter glass vessel; the cathode was a copper plate 80 × 120 mm. In the anode section we placed a solution of 25 g of butynediol in 550 ml of 15% sulfuric acid; in the cathode section, 15% sulfuric acid. A current strength of 3-3.5 A was passed through the electrolyzer at a voltage on the terminals of 5 V in the course of 24 hr. The temperature of the anode section was kept at 10-14° by water cooling of the anode. Then the anode liquid was saturated with sodium chloride and extracted with ether for eight hours in a continuous extractor. After distillation of the ether we obtained 25-27 g of acetylene dicarboxylic acid with m.p. 167-172° (decomposition), suitable for esterification without preliminary purification.

The dimethyl ester of acetylene dicarboxylic acid, b.p. 94-98° (19 mm), 66-67° (3 mm), 95-98° at 19 mm [15]) was obtained by the method of [15]. The diethyl ester of acetylene dicarboxylic acid, b.p. 105-107° (12 mm), 81-83° (3 mm) (106-107° at 12-13 mm [16]) was obtained by esterification with removal of water as a ternary azeotropic mixture (alcohol–water–toluene) [16, 17]. The periodic method of azeotropic distillation was replaced by a continuous method, using a rectification column with an attachment for complete condensation.

• The structure of the addition products should finally be established by further chemical studies.

Compound number	Name	M.p.	Yield, %	Empirical formula	% C		% H		% S	
					found	calc.	found	calc.	found	calc.
(I)	α,α'-Di(phenylsulfonyl)-succinic acid	189—190° (with decomp.)	31	$C_{16}H_{14}O_8S_2$	48.28	48.30	3.29	3.52	15.95	16.07
(II)	Dimethyl ester of α,α'-di(phenylsulfonyl)-succinic acid	172—174	38	$C_{18}H_{18}O_8S_2$	50.45	50.75	4.11	4.23	15.10	15.06
(III)	Diethyl ester of α,α'-di(phenylsulfonyl)-succinic acid	124—126	34	$C_{20}H_{22}O_8S_2$	52.74	52.80	4.77	4.84	14.03	14.10
(IV)	α,α'-Di(p-tolylsulfonyl)-succinic acid	182—184 (with decomp.)	33	$C_{18}H_{18}O_8S_2$	50.51	50.75	4.01	4.23	15.00	15.05
(V)	Dimethyl ester of α,α'-di(p-tolylsulfonyl)-succinic acid	170—172	67	$C_{20}H_{22}O_8S_2$	52.90	52.80	4.88	4.83	14.06	14.10
(VI)	Diethyl ester of α,α'-di(p-tolylsulfonyl)-succinic acid	164—166	95	$C_{22}H_{26}O_8S_2$	54.74	54.70	5.44	5.40	13.30	13.28
(VII)	α,α'-Di(p-nitrophenylsulfonyl)-succinic acid	192—194 (with decomp.)	76	$C_{16}H_{12}O_{12}N_2S_2$ *	39.51	39.33	2.61	2.46	12.89	13.20

* Found %: N 5.65. Calculated %: N 5.73.

Sulfinic acids: benzenesulfinic, m.p. 83-84° (83-84° [18]), p-toluenesulfinic, m.p. 88-91° (about 90° [19]), and p-nitrobenzenesulfinic acid, m.p. 158° (with decomposition) (159° with decomposition [20]) were obtained by reduction of the corresponding sulfonyl chlorides with sodium sulfite [21].

α,α'-Di(arylsulfonyl)-succinic acids (I, IV, VII). We dissolved 0.02 g mole of sulfinic acid by heating to 50° in glacial acetic acid and to the resulting solution with stirring added 1.4 g (0.0125 g mole) of acetylene dicaboxylic acid in 5 ml of glacial acetic acid. The crystalline precipitate was filtered off after standing for a day, dried, and recrystallized from glacial acetic acid.

Esters of α,α'-di(arylsulfonyl)-succinic acid (II, III, V, VI). To 0.01 g mole of sulfinic acid dissolved in methanol by heating to 40° we added with stirring a methanol solution of 0.01 g mole of the corresponding ester of acetylene dicarboxylic acid. After keeping for 30 min at 40°, the reaction mass was allowed to stand at room temperature. After a day the crystalline precipitate was filtered off, dried, and recrystallized from alcohol.

α,α'-Di(arylsulfonyl)-succinic acids and their esters were colorless, crystalline substances, soluble in alcohol and glacial acetic acid, more difficultly so in benzene, insoluble in water.

Hydrolysis of the esters of α,α'-di(arylsulfonyl)-succinic acids. We heated to boiling 0.482 g (0.001 g mole) of the diethyl ester of α,α'-di(p-tolylsulfonyl)-sulfinic acid (VI) in 10 ml of 1 N KOH. The resulting solution was boiled for three hours. After cooling and acidifying with 2 N hydrochloric acid we added to the solution 0.216 g (0.02 g mole) of benzoquinone and stirred for 30 min at 50-55°. Then the light brown precipitate of 2,5-dihydroxy-4'-methyldiphenylsulfone (adduct of p-toluenesulfinic acid and benzoquinone) was filtered and dried. Yield 3.4 g (65%), m.p. 210-212° (decomposition). After recrystallization from dilute alcohol, colorless prisms with m.p. 212-213° (211-212° [6b]).

Found %: C 59.12; H 4.72; N 12.06. Calculated %: C 59.15; H 4.58; N 12.13.

In the hydrolysis of the diethyl ester of α,α'-di(phenylsulfonyl)-succinic acid (III) we obtained 2,5-dihydroxydiphenyl sulfone with m.p. 196° (196° [6a]).

The infrared spectra* were taken on an IKS-12 spectrograph for compounds (I), (II), (IV), and (V) in the crystalline state (NaCl prism). In the region of 4.5-7 μ the substances were taken in a paste with prefluorinated hydrocarbons, and in the region of 7-12 μ in a paste with vaseline oil.

(I), see figure.
(II) 1740 (s), 1546 (w), 1434 (s), 1335 (s), 1260 (s), 1204 (m), 1150 (s), 1084 (m), 1004 (m), 870 (s), 825 (m)
(IV) 1716 (s), 1579 (w), 1407 (s), 1335 (s), 1290 (m), 1154 (s), 1087 (m), 912 (w), 841 (w), 819 (m)
(V) 1731 (s), 1596 (w), 1434 (w), 1374 (w), 1324 (s), 1297 (s), 1150 (s), 1084 (m), 982 (m), 882 (s), 817 (m).

SUMMARY

We have shown that like benzoquinone, acetylene dicarboxylic acid and its esters add to their multiple bonds the arylsulfinic acids, with formation of disulfones.

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ADDITION REACTIONS OF ACETYLENE CARBOXYLIC ACIDS AND THEIR ESTERS

II. REACTIONS WITH CYCLIC THIOAMIDES

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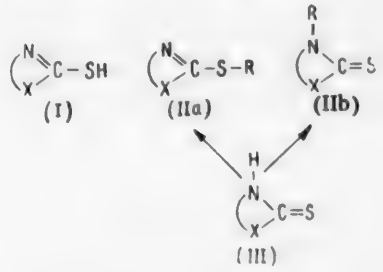
2-Mercaptobenzthiazole, 2-mercaptobenzimidazole, and similar heterocyclic mercapto compounds which contain the grouping of atoms (I) show a double reactivity: depending on the conditions of carrying out the reaction they give alkyl derivatives of either the thiol (IIa) [1, 2] or the thione (IIb) [3, 4] form.



A study of the infrared spectra of a series of mercapto compounds with structure (I) has shown that in the crystalline state and in solution these compounds are thiones and can be considered as cyclic thioamides (III) [5-7]. Thus, 2-mercaptobenzthiazole and 2-mercaptobenzimidazole are actually cyclic thioamides: benzothiazole-2-thione and benzimidazole-2-thione.

It is possible that in solution these compounds establish a tautomeric equilibrium thione $\rightleftharpoons$ thiol, which is so shifted to the thione form that the thiol form cannot be detected by the spectrum method. According to A. N. Nesmeyanov and M. I. Kabachnik [8, 9], in such a tautomeric equilibrium A $\rightleftharpoons$ B where form A greatly predominates over form B, the derivative B' is formed not from B by scheme (1), but from A by scheme (2) according to the mechanism of "transfer of reaction center."

$$\underset{(1)}{A \rightleftharpoons B \longrightarrow B'} \qquad \underset{(2)}{B' \longleftarrow A \rightleftharpoons B}$$

According to this, in the case of a cyclic thioamide the thiol derivatives (IIa) could be formed from the thione (III) by scheme (2). But, since the alkyl derivative (IIa) is obtained by the action of alkylating agents in an alkaline medium where the substance reacts as a thiol salt, the formation of a sulfide in the alkylation cannot be considered as evidence of reaction of the cyclic amide according to scheme (2). Therefore it is of interest to test the possibility of obtaining thiol derivatives (IIa) starting from the thione (III) under conditions which exclude the existence of a shift in the equilibrium toward the thiol form (I), that is, in a neutral or weakly acid medium.

For this purpose it seemed most suitable to study the reaction of cyclic thiones with α,β-acetylene carboxylic acids which, as is known, can react smoothly at the triple bond with substances which contain the thiol group to form sulfides [10-15]. Cyclic thioamides (2-benzthiazolethione and 2-benzimidazolethione) are only potential thiols and in a neutral medium can give sulfides only if they can react by scheme (2).

We first studied the reaction of 2-benzthiazolethione and 2-benzimidazolethione with propiolic acid [16] and its ethyl ester, and also with acetylene dicarboxylic acid [17, 18] and its dimethyl and diethyl esters.

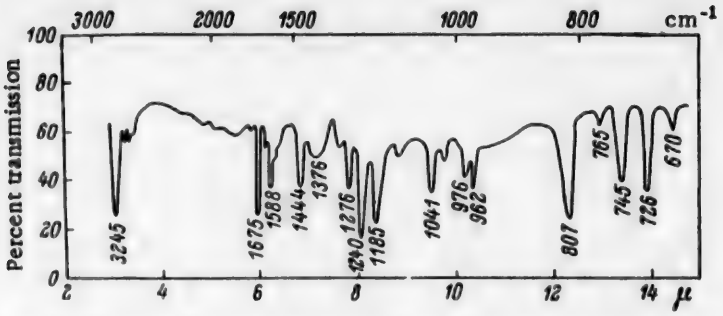


Fig. 1. Infrared absorption spectrum of the ethyl ester of β-(2-benzimidazolethio)-acrylic acid (VII).

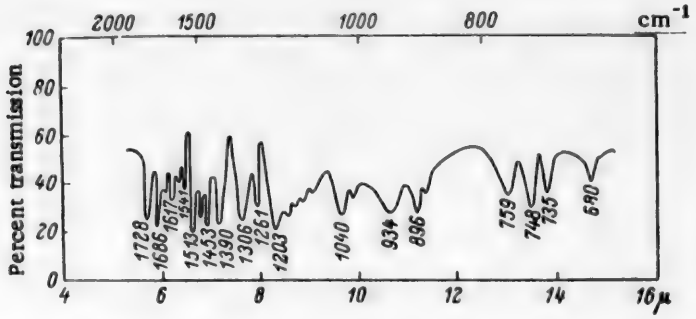
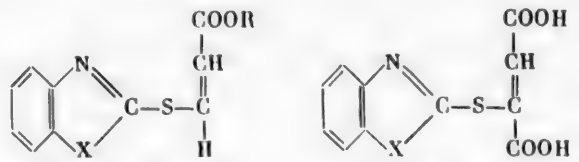


Fig. 2. Infrared absorption spectrum of 2-carbethoxymethylenethiazolidin-3-one-(3,2-a)benzimidazole (XIV).

The reaction of 2-benzothiazolethione and 2-benzimidazolethione with acetylene carboxylic acids and their esters was carried out in anhydrous alcohol, ethyl acetate, and acetic acid in the cold or with heating.

It was shown that thiones react smoothly with propiolic acid and its ester and also with acetylene dicarboxylic acid, forming good crystalline colorless or light yellow products. As the result of analysis showed, they are products of addition of one molecule of thione to the triple bond of the corresponding acid or ester (IV-IX).



(IV) X = S, R = H;
(V) X = S, R = C_2H_5;
(VI) X = NH, R = H;
(VII) X = NH, R = C_2H_5.

(VIII) X = S;
(IX) X = NH.

The structures of these adducts were confirmed by study of their infrared spectra.

In the spectra of compounds (IV, VII, VIII, IX) there was an intense absorption band in the region 700-670 cm^{-1} which belonged to the valence oscillation of the sulfide group [19], and also a band in the region 960-920 cm^{-1} which belonged to the nonplanar deformation oscillation of the C – H in the group $\rangle C = CH-$ in the trans-position of the substituent [20] (Fig. 1).

From these results it follows that the sulfides (IV-IX) evidently have a trans-configuration, and especially compounds (VIII) and (IX) are derivatives of fumaric acid * (table).

* The following facts also agree with this conclusion: illumination of a water solution of the sodium salt of dicarboxylic acid (VIII) with ultraviolet light in the presence of a trace of bromine, under conditions of transformation of maleic to fumaric acid [21] does not change the starting substance.

Addition Products (IV-IX)

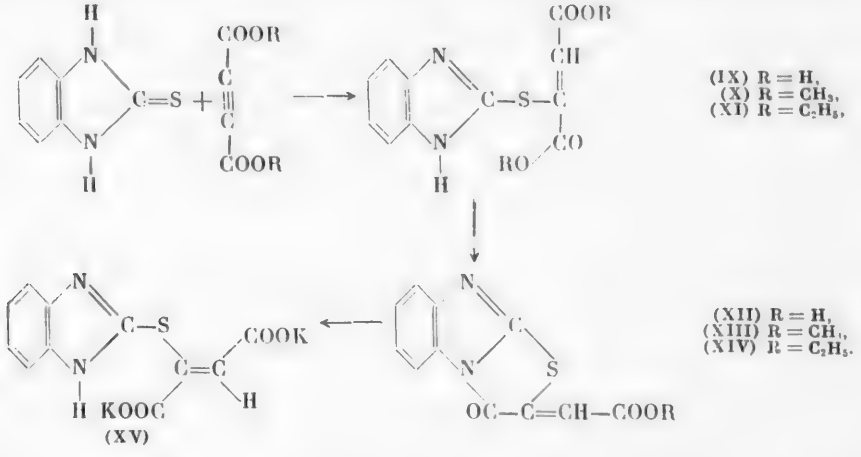
Compound No.	Name	M.p.	Yield, %	Empirical formula	% N		% S	
					found	calc.	found	calc.
(IV)	β-(2-Benzthiazolylthio)-acrylic acid	190—191° (decomp.)	57	$C_{10}H_7O_2NS_2$ *	5.70	5.89	27.15	26.96
(V)	Ethyl ester of β-(2-benzthiazolylthio)-acrylic acid	78—80	55	$C_{12}H_{11}O_2NS_2$ **	5.05	5.28	24.31	24.10
(VI)	β-(2-Benzimidazolylthio)-acrylic acid	198—200 (decomp.)	63	$C_{10}H_8O_2N_2S$	12.72	12.73	14.50	14.51
(VII)	Ethyl ester of β-(2-benzimidazolylthio)-acrylic acid	177—178	89	$C_{12}H_{12}O_2N_2S$	11.37	11.22	12.94	12.80
(VIII)	2-Benzthiazolylthiofumaric acid	154—156 (decomp.)	67	$C_{11}H_7O_4NS_2$	5.22	4.98	22.73	22.75
(IX)	2-Benzimidazolylthiofumaric acid	196—197 (decomp.)	70	$C_{11}H_8O_4N_2S$	10.76	10.60	12.16	12.12

* Found %: C 50.81; H 2.83. Calculated %: C 50.60; H 2.95.

** Found %: C 54.33; H 4.35. Calculated %: C 54.30; H 4.15.

For the adduct (IV-VII) we assume addition of the thione on the β-carbon of the propiolic acid and its ester (and not on the α-carbon) by analogy with the numerous previously described additions of mercaptans to propiolic acid [10-13].

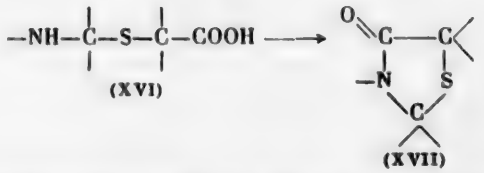
In the reaction of 2-benzimidazolethione with esters of acetylene dicarboxylic acid there are formed well crystallized, bright yellow substances which, to judge by analysis and the transformations described below can be assigned the tricyclic structure of esters of thiazolidine-3-one-(3,2-a)-benzimidazole 2-methylene carboxylic acid (XIII, XIV).



(XV)

In the infrared spectrum of compound (XIV) there are intense absorption bands at 1728 and 1686 cm^{-1}; the first evidently belongs to the valence oscillation of the carbonyl in the α,β-unsaturated ester group [19], and the second to the lactam carbonyl of the thiazolidinone ring [19, 20] (Fig. 2).

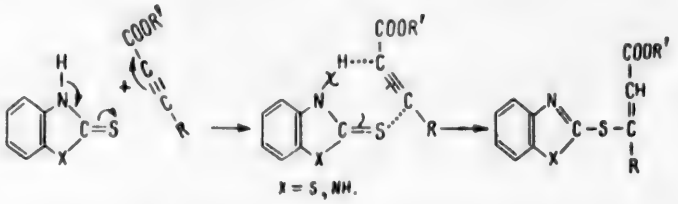
The formation of the tricyclic compounds (XIII) and (XIV) is confirmed by the observations [22, 23] that compounds which contain the system (XVI) are easily closed to form a thiazolidinone ring (XVII).



(XVI) (XVII)

In the case of addition of 2-benzimidazolethione to esters of acetylene dicarboxylic acid, the splitting out of a molecule of alcohol with formation of a five-membered thiazolidone ring* occurs spontaneously, so that we cannot isolate an uncyclized addition product (X), (XI). At the same time compound (IX), the product of the reaction of 2-benzimidazolethione with free acetylene dicarboxylic acid, is cyclized with formation of the thiazolidinone (XII) only by heating with dilute hydrochloric acid. The same substance (XII) is formed in acid hydrolysis of esters (XIII), (XIV). In alkaline hydrolysis compounds (XIII) and (XIV), like compound (XII), give salts of the dicarboxylic acid (XV), that is, there is not only hydrolysis of the ester group, but also an opening of the thiazolidinone ring at the amide $\rangle$ N–CO bond.

As the above discussion shows, 2-benzothiazolethione and 2-benzimidazolethione give with acetylene carboxylic acids and their esters addition products with a sulfide structure, that is, derivatives of the thiol form. The conditions of carrying out the reaction make impossible the existence of a shift in the equilibrium thione $\rightleftharpoons$ thiol toward the thiol form, that is, formation of the thiol derivatives from thiones in this case takes place by scheme (2). It can be assumed that the mechanism of the reaction is through an intermediate cyclic complex [24, 25] as shown in the following scheme:



X = S, NH.

Evidently some other reactions of the cyclic thioamides in which thiol derivatives are formed also occur by the mechanism of formation of intermediate cyclic active complexes without the preliminary formation of a tautomeric thiol form.

EXPERIMENTAL

Acetylene carboxylic acids and their esters. Propiolic acid, b.p. 53-55° (12 mm) [16] was obtained by oxidation of propargilic alcohol with chromic anhydride. Ethyl propiolate, b.p. 116-118° [26] was obtained by esterification of the acid with azeotropic removal of water [18].

Acetylene dicarboxylic acid, m.p. 175-176° (decomposition) [17] was obtained from dibromosuccinic acid [17]. For esterification we used acetylene dicarboxylic acid with m.p. 167-170° (decomposition), obtained by electrochemical oxidation of butynediol [18]. The dimethyl ester of acetylene dicarboxylic acid, b.p. 94-98° (19 mm), 66-67° (3 mm) was obtained by the method of [27]; the diethyl ester, b.p. 105-107° (12 mm), 81-83° (4 mm) [28] was obtained by the method of [18].

β-(2-Benzthiazolylthio)-acrylic acid (IV). In a solution of 0.7 g of propiolic acid in 30 ml of anhydrous alcohol was placed 1.67 g of 2-benzthiazolethione and the resulting mixture was heated to boiling of the solvent. The solution was boiled under reflux for 2.5 hr and stood at room temperature. After several minutes a precipitate began

* The closing of the ring is little likely because of the α-carboxyalkyl group in the six-membered thiazinone ring; otherwise it would occur in the reaction of 2-benzimidazolethione with propiolic esters. Actually, under the same conditions, when only a six-membered ring can be formed (and not a five-membered one) adduct (VII) is not cyclized.

to appear. We obtained 1.35 g of a yellow crystalline powder with m.p. 188-190° (decomposition). After recrystallization from methanol with addition of activated charcoal, yellow needles with m.p. 190-191° (decomposition).

Ethyl ester of β-(2-benzthiazolylthio)-acrylic acid (V). This was obtained like (IV). Precipitation began after partial evaporation. From 0.98 g of ethyl propiolate and 1.67 g of 2-benzthiazolethione we obtained 1.45 g of yellow needles with m.p. 75-79°. After recrystallization from methanol, m.p. 78-80°.

β-(2-Benzimidazolethio)-acrylic acid (VI). To a solution of 0.7 g of propiolic acid in 3 ml of ethyl acetate was added with stirring 1.5 g of 2-benzimidazolethione. The mixture was heated on a water bath to boiling of the solvent and left at room temperature. We obtained 1.4 g of yellowish powder with m.p. 190-191° (decomposition). After recrystallization from methyl alcohol, colorless, glittering, finely crystalline powder with m.p. 198-200° (decomposition).

Ethyl ester of β-(2-benzimidazolethio)-acrylic acid (VII). Obtained like (IV). From 0.98 g of ethyl propiolate and 1.5 g of 2-benzimidazolethione we obtained 2.2 g of light brown platelets with m.p. 173-175°. After recrystallization from alcohol, glittering, colorless plates, m.p. 177-178°.

2-Benzothiazolylthiofumaric acid (VIII). To a solution of 1.14 g of acetylene dicarboxylic acid in 5 ml of ethyl acetate was added with stirring 1.67 g of 2-benzothiazolethione in 50 ml of ethyl acetate. The reaction mixture was heated until a solution formed and left at room temperature. After several minutes precipitation began. We obtained 1.9 g of yellow powder, m.p. 150-152° (decomposition). After recrystallization from methanol, yellow, finely crystalline powder, m.p. 154-156° (decomposition).

2-Benzimidazolethiofumaric acid (IX). Obtained like (VIII). From 1.14 g of acetylene dicarboxylic acid and 1.5 g of 2-benzimidazolethione we obtained 1.85 g of colorless, finely crystalline powder with m.p. 195-197° (decomposition). The substance was purified by repeated washing on the filter with hot alcohol.*

2-Carbomethoxymethylene thiazolidine-3-one-(3,2-a)benzimidazole (XIII). We added by drops with energetic stirring 1.42 g of the dimethyl ester of acetylene dicarboxylic acid to 1.5 g of 2-benzimidazolethione in 10 ml of glacial acetic acid. Dropping was accompanied by heating of the reaction mass. Then the mixture was heated on a water bath to full solution of the precipitate. We obtained 1.7 g (65%) of a yellow powder with m.p. 180-185° (decomposition). After recrystallization from acetone, glittering orange prisms, m.p. 190-192°.

Found %: C 57.19; H 3.64; N 10.87; S 10.03. $C_{12}H_8O_3N_2S$. Calculated %: C 56.94; H 3.65; N 10.76; S 10.22.

2-Carbethoxymethylene thiazolidine-3-one-(3,2-a)-benzimidazole) (XIV). Obtained like compound (XIII). From 1.7 g of diethyl ester of acetylene dicarboxylic acid and 1.5 g of 2-benzimidazolethione, we obtained 1.6 g (58%) of a yellow powder with m.p. 155-160° (decomposition). After recrystallization from acetone, glittering yellow needles, m.p. 168-170°.

Found %: N 12.27; S 11.59. $C_{13}H_{10}O_3N_2S$. Calculated %: N 12.30; S 11.68.

Hydrolysis of 2-carbethoxymethylene thiazolidine-3-one-(3,2-a)-benzimidazole (XIV). a) In the presence of acid. To 0.548 g of ester (XIV) was added 20 ml of 20% hydrochloric acid and the resulting mixture was refluxed for three hours. The precipitate which came down after cooling was filtered off and washed with water. We obtained 0.36 g (73%) of 2-carboxymethylene thiazolidine-3-one-(3,2-a)-benzimidazole (XII) in the form of yellow needles with m.p. 214-215° (decomposition).

Found %: N 11.60; S 12.97. $C_{11}H_6O_3N_2S$. Calculated %: N 11.38; S 13.00.

b) Hydrolysis in the presence of alkali. A weight of 0.548 g of (XIV) in 15 ml of 1 N potassium hydroxide was heated gently to the formation of a bright yellow solution. After cooling, the solution was treated with 2 N hydrochloric acid to an acid reaction to Congo. The precipitate was filtered off and washed with water. We obtained 0.48 g (91%) of colorless needles, m.p. 197-198° (decomposition). The substance was shown by mixed melting point to be identical with 2-benzimidazolylthiofumaric acid (IX).

The infrared spectra** was taken on an IKS-12 spectrograph for compounds (IV, VII, IX, XIV) in the crystalline state (in a paste with perfluorinated hydrocarbons in the region 2.5-7 μ and in a paste with vaseline oil in the

* The substance could not be recrystallized from the ordinary solvents. In attempts to recrystallize (IX) from dilute hydrochloric acid the cyclic acid (XII) was formed; an analogous result was obtained in attempts to purify (IX) by reprecipitation.

** The spectra were taken by L. F. Trefilova.

region 7-14.5 μ). The spectrum of substance (VII) was taken in the region 2.5-14.5 μ (Fig. 1); the spectra of the other substances were taken in the region 4.5-14.5 μ; we used a LiF prism (2.5-4.5 μ) and NaCl (4.5-14.5 μ).

(IV) 1678 (s), 1576 (s), 1560 (s), 1427 (m), 1344 (m), 1314 (w), 1256 (m), 1172 (m), 1085 (w), 1024 (w), 1002 (m), 921 (w), 808 (w), 762 (w), 698 (w) cm^{-1}.

(VIII) 1692 (s), 1610 (m), 1416 (m), 1322 (s), 1254 (v.s.), 1081 (w), 1042 (w), 942 (w), 884 (w), 788 (w), 755 (w), 726 (w), 690 (w) cm^{-1}).

(IX) 1698 (s), 1510 (w), 1456 (m), 1289 (w), 1211 (m), 995 (w), 920 (w), 808 (w), 770 (w), 692 (w) cm^{-1}.

(VII) and (XIV)—see Figs. 1 and 2.

SUMMARY

1. We have showed that cyclic thioamides: 2-benzothiazolethione and 2-benzimidazolethione add to the triple bond to propiolic and acetylene dicarboxylic acids and their esters to form unsaturated sulfides. The addition products of 2-benzimidazolethione to acetylene dicarboxylic acid and its esters cyclize into thiazolidinebenzimidazoles.

2. We suggest a mechanism of addition of cyclic thioamides at the triple bond with formation of sulfides without intermediate conversion of the thioamides into the thiol form.

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ADDITION REACTIONS OF ACETYLENE CARBOXYLIC ACIDS AND THEIR ESTERS

III. REACTIONS WITH CYCLIC AMINES AND β,β'-DICHLORODIETHYLAMINE

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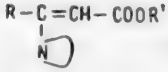
It is known that amines react smoothly with esters of acetylene carboxylic acids (EACA), to give unsaturated compounds with the amine portion in the β-position to the carbalkoxy group [1].

$$R{-}C{\equiv}C{-}COOR' + HNR_1R_2 \longrightarrow R{-}C(NR_1R_2){=}CH{-}COOR'$$

In this reaction, as in a number of other addition reactions [2], EACA behave like benzoquinone, which can also add amines at the conjugated double bonds of the ring [3]. Considering this similarity in the addition reaction of amines to EACA and to benzoquinone, we tried to carry out the reaction of EACA with cyclic secondary amines; ethylene imine, pyrrolidine, and morpholine. There was particular interest in the addition of ethylene imine, since it is known that some addition products of ethylene imine to benzoquinone have considerable anticancer activity [4].

For the reaction with these amines we took esters of propiolic, tetrolic, phenylpropiolic, and acetylene dicarboxylic acids. Since amines react with EACA with warming, the reaction was carried out with cooling and gradual addition of amines and EACA. The most energetic reaction among the amines was with ethylene imine, and among the EACA, with the ester of acetylene dicarboxylic acid. As a result of the reaction, shown by analysis of the products, monoadducts were formed; their structure could be expressed by the following formula:



(I)

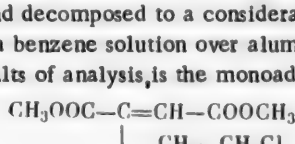
where N⟨ is the cyclic amine residue.

The list of compounds obtained (Nos. 1-13), their analyses and constants are given in Tables 1 and 2.

The addition products of ethylene imine to EACA are colorless, viscous oils (Nos. 1-4), which distill in a vacuum with slight decomposition. The reaction product of ethylene imine with the ester of acetylene dicarboxylic acid (No. 4) is partly converted, after holding, into a crystalline substance (No. 5), which has the same elementary composition as the oil (No. 4). The crystalline substance is probably the trans-form of the addition product, while the liquid is its acid form or a mixture of cis and trans forms. The reaction products of the ethylene imine with the other acetylene carboxylic esters (Nos. (1-3) under the same conditions remain as oils and, as the spectroscopic evidence indicates, are probably cis-isomers with small admixtures of the trans-form.

In the reaction of EACA with pyrrolidine and morpholine, viscous oils are also obtained (Nos. 6-13), distilling in a narrow range. However, in distinction from compounds 1-4 they are completely transformed into crystalline products with low melting points; compounds 6 and 11 crystallize especially rapidly.

The ease with which EACA reacts with cyclic secondary amines, especially with ethylene imine, led us to test the possibility of addition of another cytotoxic amine, β,β'-(dichlorodiethyl)-amine, to the ester of acetylene dicarboxylic acid. As a result of the reaction we obtained a thick, slightly mobile oil with a light brown color, which in vacuum distillation darkened strongly and decomposed to a considerable extent. The oil, purified without preliminary distillation by chromatography from a benzene solution over aluminum oxide, gave after distillation of the solvent a thick product which, from the results of analysis, is the monoadduct (II).



(II)

TABLE 1. Addition Compounds of Ethylene Imine

Comp. No.	R	R'	Name	B.p.	n_D^{20}	d_4^{20}	Yield, %	Found, %			Empirical formula	Calc., %		
								C	H	N		C	H	N
1	H	C_2H_5	Ethyl ester of β-(N-ethylenimino)-acrylic acid	65—67° (3)	1.4843	1.0277	51	59.83	8.10	9.41	$C_7H_{11}O_2N$	59.60	7.80	9.93
2	CH_3	C_2H_5	Ethyl ester of β-(N-ethylenimino)-crotonic acid	75—76 (3)	1.4938	1.0040	59	62.07	8.60	9.31	$C_8H_{13}O_2N$	61.80	8.38	9.04
3	C_6H_5	C_2H_5	Ethyl ester of β-(N-ethylenimino)-cinnamic acid	135—136 (3)	1.5673	1.0817	71	71.85	6.95	6.46	$C_{13}H_{15}O_2N$	71.90	6.92	6.45
4	$COOCH_3$	CH_3	Dimethyl ester of ethylenimino-maleic acid	104—106 (2.5)	1.4950	1.1878	24	—	—	7.52	$C_8H_{11}O_4N$	—	—	7.57
5	$COOCH_3$	CH_3	Dimethyl ester of ethylenimino-fumaric acid	M.p. 1—72	—	—	16	51.52	6.11	7.56	$C_8H_{11}O_4N$	51.80	5.95	7.57

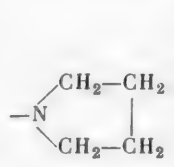
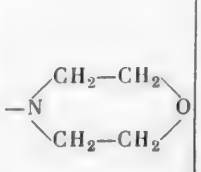
Interesting results are obtained in the study of the infrared spectra of the compounds which we synthesized. As would be expected, in the spectra of all the compounds there was no absorption band in the region 2200-2100 cm^{-1} which characterizes the valence oscillation of the $-C \equiv \underline{C}-$ group [5]. At the same time, the double bond clearly is responsible for the valence oscillation in the region 1630-1610 cm^{-1} [5], and for the crystalline substances, also for the presence of the absorption band in the region 980-960 cm^{-1}, which corresponds to the nonpolar deformation oscillation of the CH-ethylene bond in the trans-group [6].

The general form of the spectra in the region 3090-2860 cm^{-1}, which relates to the valence oscillation of CH– [5], is characterized for the compounds studied by the presence of triplet (or doublet) narrow bands, one of which has a relatively more intense absorption than the others. For the ethylene imine compounds this triplet is 3085-3075 (m), 3020-3000 (v.s.), and 2970-2900 (m) cm^{-1}. For the pyrrolidine derivatives, in accord with the decreased forces in the ring, the triplet (doublet) is shifted toward the lesser oscillation frequencies: 2990-2980 (s), 2950 (w), 2890-2870 (m) cm^{-1}. In morpholine, where the forces in the ring are still less than in pyrrolidine, the triplet is more markedly shifted: 2986-2964 (s), 2920-2010 (w), 2868-2860 (s) cm^{-1}. We determined the spectra of the compounds studied in the region 3400-2800 cm^{-1}, and for comparison, the spectra of the starting cyclic amines, whose NH groups showed valence oscillation bands in the interval 3350-3250 cm^{-1} [5] (Fig. 1). As Fig. 1 shows, each set of substances has a characteristic spectra curve. This permits the suggestion that in this region there is chiefly the oscillation of the CH-methylene groups of the heterocycle. In Fig. 2, for example, we show the infrared spectrum of compound 1, where, besides the already mentioned band of valence oscillation of C–H in the region 3080-2910 cm^{-1}, there is another characteristic absorption band. Its relation to the oscillation of the other groups is given in Table 3.

EXPERIMENTAL

Acetylene carboxylic acids and their esters. Tetrolic acid, m.p. 72-74° (74-76° [9]) was obtained from 3-methyl-5-pyrrazolone [9]. Phenylpropiolic acid, m.p. 136-138° (136-138° [10]) was obtained from dibromohydrocinnamic acid [10]. Propiolic acid, b.p. 53-55° (12 mm) (53-54.5° at 12 mm [11]) was obtained by oxidation of propargylic alcohol by chromic anhydride. Acetylene dicarboxylic acid, m.p. 167-172° (decomposition) was obtained by electrochemical oxidation of butynediol [2]. The ethyl ester of tetrolic acid, b.p. 162-164° (163-164° [12]), the ethyl ester of phenylpropiolic acid, b.p. 124° (6 mm) (124° at 6 mm [13]), and the ethyl ester of propiolic acid, b.p. 116-118° (119° [14]) were obtained by esterification of the corresponding acids with azeotropic distillation of water [2]. The dimethyl ester of acetylene dicarboxylic acid, b.p. 94-98° (19 mm) (66-67° at 3 mm [15]) was obtained according to [15].

TABLE 2. Addition Products of Pyrrolidine and Morpholine

Comp. No.	R	R′	Cyclic amine	Name	M.p.	Yield, %	Found, %			Empirical formula	Calc., %		
							C	H	N		C	H	N
6	H	C_2H_5		Ethyl ester of β-(N-pyrrolidyl)-acrylic acid	41—43°	55	63.82	8.99	8.05	$C_9H_{15}O_2N$	63.80	8.85	8.25
7	CH_3	C_2H_5		Ethyl ester of β-(N-pyrrolidyl)-crotonic acid	28—30	70	65.52	9.35	7.51	$C_{10}H_{17}O_2N$	65.55	9.28	7.72
8	C_6H_5	C_2H_5		Ethyl ester of β-(N-pyrrolidyl)-cinnamic acid	58—60	78	73.31	7.84	5.98	$C_{15}H_{19}O_2N$	73.46	7.75	5.71
9	$COOCH_3$	CH_3		Dimethyl ester of N-pyrrolidylfumaric acid	69—71	54	56.05	6.80	6.72	$C_{10}H_{15}O_4N$	56.30	7.04	6.57
10	H	C_2H_5		Ethyl ester of β-(N-morpholyl)-acrylic acid	29—31	67	58.15	8.41	7.92	$C_9H_{15}O_3N$	58.30	8.11	7.56
11	CH_3	C_2H_5		Ethyl ester of β-(N-morpholyl)-crotonic acid	31—33	69	60.26	8.56	7.31	$C_{10}H_{17}O_3N$	60.25	8.54	7.02
12	C_6H_5	C_2H_5		Ethyl ester of β-(N-morpholyl)-cinnammic acid	49—51	68	68.97	7.50	5.66	$C_{15}H_{19}O_3N$	68.98	7.28	5.37
13	$COOCH_3$	CH_3		Dimethyl ester of N-morpholylfumaric acid	57—59	52	52.29	6.67	5.85	$C_{10}H_{15}O_5N$	52.48	6.54	6.11

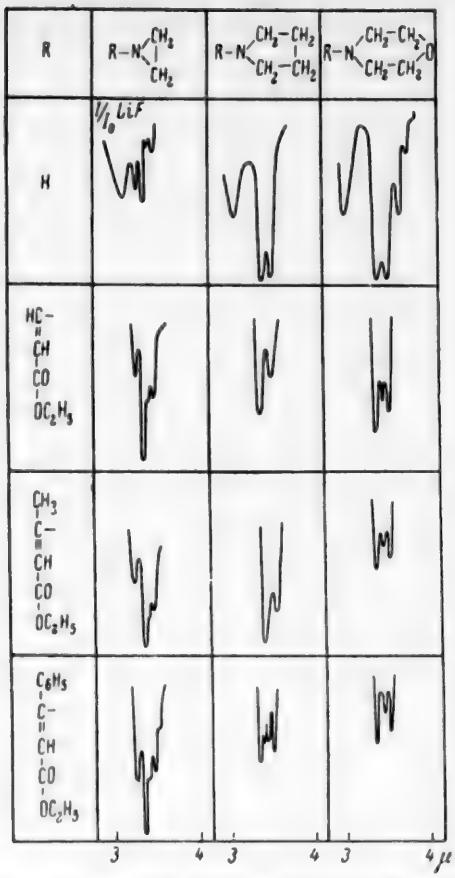


Fig. 1. Infrared absorption spectra of compounds 1-3, 5-13 in the region 3-4 μ.

Addition products of ethylene imine (Nos. 1-5, Table 1). To 0.1 g mole of acetylene carboxylic esters was added dropwise with stirring and ice cooling 0.33 g mole of ethylene imine. Then the reaction mixture was heated for three hours on a water bath at 40 to 60° and kept for 12 hr at room temperature, then vacuum distilled. Compounds 1-4 were colorless oils with a characteristic amine odor; easily soluble in alcohol and ether, insoluble in water. The addition product of ethylene imine to dimethyl acetylene dicarboxylate (compound 4) after being kept for two weeks at 25° was placed in a refrigerator (−5°) and partly crystallized. From the precipitate, filtered and recrystallized from ligroin, we obtained colorless, needle like crystals (compound 5) with m.p. 71-72°. The filtrate was an oil identical with compound 4.

Addition products of pyrrolidine and morpholine (Nos. 6-13, Table 2). To 0.1 g mole of acetylene carboxylic ester was added 0.1 g mole of the corresponding amine with shaking and cooling. After heating for three hours on a boiling water bath and keeping at room temperature for 12 hr, the reaction mass was vacuum distilled. The resulting colorless oil stood for 10 days at 12° and crystallized completely, except for compounds 6 and 10, which crystallized immediately after distillation. After recrystallization from ligroin substances 6-13 were colorless, needlelike crystals, soluble in alcohol and ether, difficultly soluble in ligroin, insoluble in water.

Dimethyl Ester of N-(β,β'-Dichlorodiethyl)-amino-maleic acid(?)* (II)

To 1.42 g (0.01 g mole) of dimethyl acetylenedicarboxylate with shaking and cooling was added dropwise 1.42 g (0.01 g mole) of β,β'-dichlorodiethylamine. Then the reaction mixture was heated for three hours on a water bath at 30-40° and kept 12 hr at room temperature; it was then extracted with benzene. The benzene

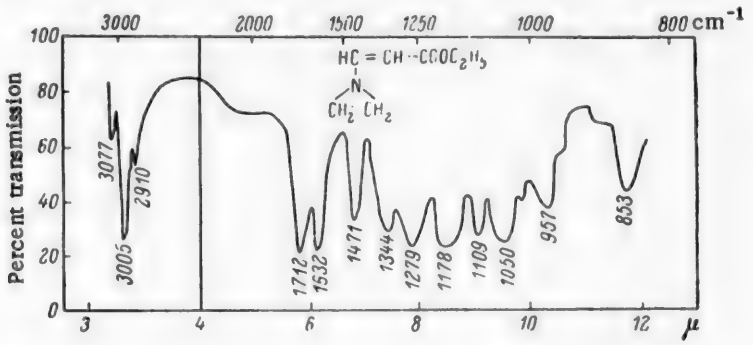


Fig. 2. Infrared absorption spectrum of the ethyl ester of β-(N-ethyl-enimino)-acrylic acid in the region 2.5-13 μ.

extract was chromatographed over aluminum oxide. After evaporation of the eluate we obtained 2.2 g (78%) of a light colored, viscous oil, $n^{20}D$ 1.5306, d^{20}_4 1.2993, soluble in chloroform and insoluble in water.

Found %: C 42.05; H 5.23; N 5.29; Cl 24.49. $C_{10}H_{15}O_4NCl_2$. Calculated %: C 42.25; H 5.28; N 4.93; Cl 25.00.

* Spatial configuration not established.

TABLE 3. Infrared Spectrum Data for the Ethyl Ester of β-(N-ethylenimino)-acrylic Acid

Absorption bands (cm^{-1})	Belonging to group
3077 (w) 3005 (s) 2910 (w)	Valence oscillation of CH (in particular in CH_2 group of heterocycle) [5]
1712 (s)	Valence oscillation of CO group of α, β-unsaturated acid [7]
1632 (s)	Valence oscillation of $>C=C<$ [5]
1471 (m)	Shearing oscillation of CH_2 groups [6]
1344 (m) 1178 (m)	Oscillation of CH_2 groups [6]
957 (m)	Deformation oscillation of CH in grouping $>C=CH/$ (trans) [6]
853 (m)	Deformation oscillation of three membered ethylene imine ring [8]

Infrared spectrum. 3120 (m), 3005 (w), 2965 (s), 2855 (m), 1744 (S), 1709 (s), 1588 (s), 1462 (m), 1430 (m), 1318 (s), 1249 (s), 1206 (m), 1169 (s), 1049 (m), 965 (m), 936 (m), 805 (m).

The infrared spectra of all the compounds were taken in the region 2,5-13 μ (from 2.5 to 4.5 μ with a LIF prism, and from 4.5-13 μ with a NaCl prism). Compounds 1-4, 7, 10-13, and (II) were measured in the pure form, compounds 5, 6, 8, 9 in a paste with perfluorinated hydrocarbons in the region from 2,5-7μ and in a paste with vaseline oil in the region from 7-13 μ.

No. 1, see Fig. 2.

No. 2, 3071 (s), 3004 (s), 2941, 2912 (w), 1705 (s), 1626 (s), 1280 (s), 1205 (s), 1150 (s), 1062 (s), 978 (w), 990 (w), 892 (w), 844 (w).

No. 3, 3085 (m), 3004 (s), 2945, 2902, 2870 (w), 1705 (s), 1610 (s), 1446(m), 1278 (s), 1160 (s), 1446 (m), 1278 (s), 1160 (s), 1050 (m), 977 (w), 925 (w).

No. 4, 3475 (m), 3345 (s), 3080 (m), 3020 (s), 2963, 2910 (w), 1740 (s), 1705 (s), 1610 (s), 1446(m), 1728 (s), 1203 (m), 1160 (s), 1103 (m), 1050 (m), 977 (w), 857 (w).

No. 5, 3020, 2970 (w), 1728 (s), 1705 (s), 1603 (m), 1437 (m), 1289 (w), 1206, 1170 (s), 1104 (m), 1052 (m), 1030 (m), 975 (w), 958 (w), 882 (m), 852 (m), 824 (w).

No. 6, 2985 (m), 2878 (m), 1685 (m), 1643 (m), 1245 (w), 1194 (w), 1152 (s), 1123 (w), 1056 (m), 992 (m), 787 (m).

No. 7, 2993 (m), 2886 (m), 1673 (s), 1557 (w), 1308 (w), 1146 (s), 1061 (m), 1033 (s), 980 (w), 866 (w), 791 (m).

No. 8, 2990 (m), 2877 (m), 1700 (s), 1563 (s), 1328 (m), 1187 (w), 1134 (s), 1117 (s), 1047 (m), 996 (m), 975 (m), 792 (m).

No. 9, 2980 (w), 2957 (w), 2890 (w), 1740 (s), 1685 (s), 1610 (m), 1466 (m), 1352 (m), 1227 (m), 1194 (w), 1162 (s), 1123 (s), 1040 (s), 988 (m), 962 (m).

No. 10, 2986 (m), 2910 (m), 2868 (m), 1695 (s), 1616 (s), 1461 (m), 1270 (m), 1242 (s), 1197 (m), 1181 (s), 1156 (s), 1091 (s), 1061 (m), 995 (m), 980 (m), 940 (m), 833 (w).

No. 11, 2985 (m), 2910 (m), 2869 (m), 1689 (s), 1603 (s), 1447 (m), 1256 (s), 1134 (s), 1066 (m), 1003 (s), 936 (w), 902 (m), 801 (m).

No. 12, 2975 (m), 2910 (w), 2860 (m), 1735 (s), 1688 (m), 1582 (m), 1444 (s), 1408 (m), 1273 (s), 1129 (m), 1051 (s), 999 (m), 925 (m), 895 (m), 871 (m).

No. 13, 2980 (m), 2921, 2874 (m), 1740 (s), 1694 (s), 1582 (m), 1437 (m), 1428 (m), 1283 (m), 1220 (s), 1169 (s), 1123 (s), 1036 (s), 971 (m), 952 (m), 887 (m), 806 (m).

SUMMARY

We have shown that ethylene imine, pyrrolidine, morpholine, and also β,β'-dichlorodiethylamine add to the triple bond of esters of acetylene carboxylic acids with formation of unsaturated monoadducts. We have obtained 14 undescribed addition products and have studied their infrared spectra.

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THE SYNTHESIS OF NEW ARYL DERIVATIVES OF 1, 3, 4-OXADIAZOLE

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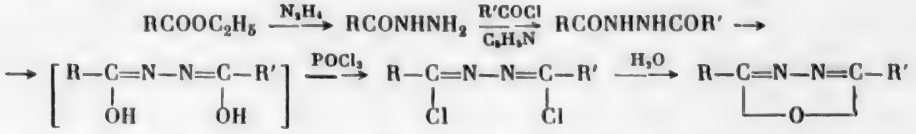
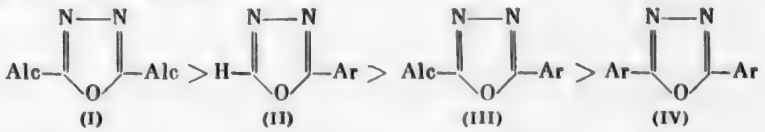
In recent years derivatives of 1,3,4-oxadiazole have found wide use as effective scintillation materials in liquids [1-3] and plastics [4-6]. Especially promising in this respect are the aryl derivatives of 1,3,4-oxadiazole [2,5,6], and therefore, in order to seek for new scintillators we have synthesized a series of new mixed 2,5-diaryl derivatives of 1,3,4-oxadiazole according to the scheme:



where R and R' are methyl, phenyl, 1-naphthyl, 2-naphthyl, 4-biphenylyl, 2-fluorenyl, 9-fluorenyl, and 9-phenanthryl.

This scheme of synthesis has been sufficiently well worked out [7, 8], but the steps in formation of oxadiazole and its isolation from a water solution in which it is prepared are of considerable interest. It is known that the solubilities of various oxadiazole derivatives in water are not the same, and in large measure depend on the substituents present, decreasing in the following order:



(I) (II) (III) (IV)

Thus, while 2,5-dimethyl-1,3,4-oxadiazole mixes with water in all proportions [9], the solubility in water of 2,5-diphenyl-1,3,4-oxadiazole is only 0.03%.

On the other hand, it was previously established [9-12] that when aqueous solutions of acids and alkalis act on oxadiazole derivatives, there is rupture of the heterocyclic ring with formation of the corresponding diarylhydrazide. A detailed study of this question which we undertook showed that the ability of oxadiazole derivatives to hydrolyze was not the same and decreased in the above order, analogously to the solubility. Thus, while substances (I) and (II) hydrolyzed very rapidly, the rupture of the oxadiazole ring in compound (IV) required long heating. For example, 2,5-dimethyl-1,3,4-oxadiazole and 2-phenyl 1,3,4-oxadiazole in an aqueous solution of mineral acid even in the cold are instantly split with formation of the starting hydrazide, while 2-phenyl-5-(9-fluorenyl)-1,3,4-oxadiazole under these conditions is very stable; 2-methyl-5-(9-fluorenyl)-1,3,4-oxadiazole occupies an intermediate position.

Thus, in the last stages of obtaining oxadiazole derivatives two processes occur: cyclization of the oxadiazole ring and its hydrolysis, as the following scheme shows:

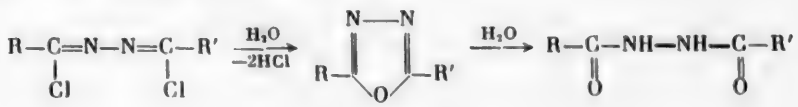


TABLE 1. Synthesized Hydrazides of the Type RCONHNHCOR'

-Hydrazide	M.p.	Yield, %	Formula	% N	
				found	calc.
1-Methyl-2-(9-phenanthryl)-	238[a]	81	$C_{17}H_{14}O_2N_2$	10.31	10.07
1-Phenyl-2-(9-phenanthryl)-	306[b]	65	$C_{22}H_{16}O_2N_2$	8.44	8.23
1-(1-Naphthyl)-2-(9-phenanthryl)-	262[c]	51	$C_{26}H_{18}O_2N_2$	7.13	7.17
1-(2-Naphthyl)-2-(9-phenanthryl)-	290[c]	48	$C_{26}H_{18}O_2N_2$	7.39	7.17
1-(4-Biphenylyl)-2-(9-phenanthryl)-	253[a]	85	$C_{28}H_{20}O_2N_2$	7.00	6.73
1,2-Di-(9-phenanthryl)-	309[d]	47	$C_{30}H_{20}O_2N_2$	6.71	6.51
1-Phenyl-2-(9-fluorenyl)-	283[c]	83	$C_{21}H_{16}O_2N_2$	8.32	8.53
1-(1-Naphthyl)-2-(9-fluorenyl)-	273[a]	30	$C_{25}H_{18}O_2N_2$	7.73	7.41
1-(2-Naphthyl)-2-(9-fluorenyl)-	257[a]	58	$C_{25}H_{28}O_2N_2$	7.57	7.41

a) From glacial acetic acid
b) From dioxane with pyridine
c) From dioxane
d) From pyridine

The rate of the second process is obviously less than the first and depends directly on the solubility of the oxadiazole.

The oxadiazoles described in the present work, like the corresponding arylhydrazides from which they are prepared, have not been described in the literature. They were all purified by repeated recrystallizations from suitable solvents to a constant melting point, followed by chromatographic purification on aluminum oxide.

2,5-Diaryl derivatives of 1,3,4-oxadiazole are colorless, crystalline substances, thermally stable except for the fluorenyl derivatives, which tar when heated; they dissolve in pyridine, dioxane, and acetic acid, more poorly in benzene, toluene, and alcohol, and are insoluble in ligroin and water.

EXPERIMENTAL

1-Methyl-2-(9-phenanthryl)-hydrazide. A mixture of 50 g of ethyl ester of 9-phenanthrene carboxylic acid and 140 ml of 98% hydrazine hydrate was heated on a boiling water bath for four hours. The 9-phenanthrene carboxylic acid hydrazide which precipitated from the reaction mass was filtered off, washed with water and alcohol and dried; yield 41.5 g (85%), m.p. 210° (228° [13]). The resulting 9-phenanthrene carboxylic acid hydrazide was boiled for one hour with 120 ml of glacial acetic acid. After cooling the solution, 39.3 g (81%) of 1-methyl-2-(9-phenanthryl)-hydrazide crystallized out; m.p. 238°. After further recrystallization from ethanol, the m.p. remained unchanged.

Found %: N 10.31. $C_{17}H_{14}O_2N_2$. Calculated %: N 10.07.

2-Methyl-5-(9-phenanthryl)-1,3,4-oxadiazole. Five g of 1-methyl-2-(9-phenanthryl)-hydrazide and 10 ml of phosphorus oxychloride were boiled in a flask with a reflux condenser to full solution of the solid, which took about 30-60 min. Then the reaction mass was cooled and 200 ml of cold water was poured in with stirring. The precipitated oxadiazole was filtered off, washed with water, and dried; yield 4.3 g (90%), m.p. 155-157°. After two recrystallizations from ethanol the yield was 2.4 g (51%), m.p. 159-160°.

Found %: N 10.93. $C_{17}H_{12}ON_2$. Calculated %: N 10.76.

TABLE 2. Synthesized Oxadiazoles of the Type R–C = N–N = C–R' (O)

1,3,4-Oxadiazole	M.p.	Yield, %	Formula	% N	
				found	calc.
2-Methyl-5-(9-phenanthryl)-	160° [e]	51	$C_{17}H_{12}ON_2$	10.93	10.76
2-Phenyl-5-(9-phenanthryl)-	187 [f]	70	$C_{22}H_{14}ON_2$	8.81	8.69
2-(1-Naphthyl)-5-(9-phenanthryl)-	171 [f]	73	$C_{26}H_{16}ON_2$	7.51	7.52
2-(2-Naphthyl)-5-(9-phenanthryl)-	208 [f]	54	$C_{26}H_{16}ON_2$	7.62	7.52
2-(4-Biphenylyl)-5-(9-phenanthryl)-	207 [f]	68	$C_{28}H_{18}ON_2$	7.31	7.03
2,5-Di-(9-phenanthryl)-	306 [e]	87	$C_{30}H_{18}ON_2$	6.87	6.63
2-Phenyl-5-(2-fluorenyl)-	154 [f]	52	$C_{21}H_{14}ON_2$	9.18	9.03
2-(1-Naphthyl)-5-(2-fluorenyl)-	212 [f]	30	$C_{25}H_{16}ON_2$	7.96	7.77
2-(2-Naphthyl)-5-(2-fluorenyl)-	168 [f]	27	$C_{25}H_{16}ON_2$	8.17	7.77
2-(4-Biphenylyl)-5-(2-fluorenyl)-	236 [f]	46	$C_{27}H_{18}ON_2$	7.39	7.25
2,5-Di-(2-fluorenyl)-	255 [g]	55	$C_{28}H_{18}ON_2$	7.20	7.04
2-Phenyl-5-(9-fluorenyl)-	263 [f]	26	$C_{21}H_{14}ON_2$	8.93	9.03
2-(1-Naphthyl)-5-(9-fluorenyl)-	182 [e]	51	$C_{25}H_{16}ON_2$	7.55	7.77
2-(2-Naphthyl)-5-(9-fluorenyl)-	165 [h]	53	$C_{25}H_{16}ON_2$	7.65	7.77

e) From ethanol
f) From benzene
g) From glacial acetic acid
h) From dioxane

1,2-Di-(9-phenanthryl)-hydrazide. Thirty g of 9-phenanthrylcarboxylic acid chloride and 100 ml of pyridine were placed in a flask fitted with a reflux condenser and mechanical stirrer, and to the resulting mixture was added with stirring 4.5 ml of 98% hydrazine hydrate. Then the reaction mass was boiled for 30 min, after which it was cooled to room temperature and distilled water was poured in. The precipitated reaction product was filtered off, washed on the filter with water, and dried; yield 19.7 g (72%), m.p. 297-300°. After two recrystallizations from pyridine the yield of hydrazide was 13 g (47%), m.p. 308-309°.

Found %: N 6.71. $C_{30}H_{20}O_2N_2$. Calculated %: N 6.51.

2,5-Di-(9-phenanthryl)-1,3,4-oxadiazole. A mixture of 12 g of 1,2-di-(9-phenanthryl)-hydrazide and 50 ml of phosphorus oxychloride was boiled in a flask with a reflux condenser for 12 hr, during which the solid did not dissolve, but only changed its outward appearance. Then the reaction product was poured into water, the crystalline precipitate was filtered off, washed with water, and dried; yield 11.4 g (90%), m.p. 305-306°. After recrystallization of the oxadiazole from ethanol with later chromatographic purification on aluminum oxide using benzene as the solvent, the yield was 10 g (87%), m.p. 306-307°.

Found %: N 6.87. $C_{30}H_{18}ON_2$. Calculated %: N 6.63.

Synthesis of 2-(2-Naphthyl)-5-(9-fluorenyl)-1,3,4-oxadiazole

1-(2-Naphthyl)-2-(9-fluorenyl)-hydrazide. To 9.5 g of 2-naphthoic acid chloride in 150 ml of dry pyridine was added with stirring 11.5 g of 9-fluorene carboxylic acid hydrazide, obtained by three hour heating on a boiling water bath of ethyl 9-fluorene carboxylate with one and a half fold excess of 98% hydrazine hydrate. After addition

of all the hydrazide the reaction mass was stirred for 20 min, then was treated with activated charcoal, filtered, and poured into 800 ml of distilled water. The precipitated reaction product was filtered, washed with water, and dried; yield 11.0 g (58%), m.p. 255°. After two recrystallization from glacial acetic acid we obtained 1-(2-naphthyl)-2-(9-fluorenyl)-hydrazide with a yield of 6.3 g (32%), m.p. 257°.

Found %: N 7.67. $C_{25}H_{18}O_2N_2$. Calculated %: N 7.41.

2-(2-Naphthyl-5-(9-fluorenyl)-1,3,4-oxadiazole. A mixture of 6 g of 1-(2-naphthyl)-2-(9-fluorenyl)-hydrazide and 40 ml of phosphorus oxychloride was boiled to full solution of the solid, which took 20-30 min, after which boiling was continued for about one hour more. Then the reaction mass was poured into one liter of water, the crystalline precipitate was filtered off, washed with water, a solution of ammonia, and again with water. After recrystallization from dioxane followed by chromatography on aluminum oxide for purification, we obtained colorless 2-(2-naphthyl)-5-(9-fluorenyl)-1,3,4-oxadiazole with m.p. 165°; yield 3 g (53%).

Found %: N 7.65. $C_{25}H_{16}ON_2$. Calculated %: N 7.77.

Analogously to the methods described above we obtained all the hydrazides and oxadiazoles which are shown in Tables 1 and 2.

SUMMARY

1. We have synthesized 23 undescribed 1,2-diarylhydrazides and 2,5-diaryl-1,3,4-oxadiazoles.
2. We have studied the tendency to hydrolyze of the various derivatives of 1,3,4-oxadiazole.

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STUDIES IN THE FIELD OF CONJUGATED SYSTEMS

CXXVIII. THE ORDER OF ADDITION OF BROMINE TO SILICON CONTAINING ENYNES*

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The order of addition of bromine to enyne hydrocarbons, homologs of vinylacetylene, depends strongly on the character and position of the radicals on the multiple bonds [1]. It is of interest to explain the effect on the reactivity of enyne systems toward bromine of substituting one of their atoms of hydrogen by a trialkyl- or triarylsilyl group.

A. D. Petrov, S. I. Sadykh-zade and others [2, 3] concluded that 1-triethylsilyl-3-buten-1-yne added the first molecule of bromine at the triple bond. This conclusion was confirmed by study of the infrared spectrum of the dibromide; frequencies of a double bond were found.

We considered it necessary to study this problem in more detail. In the present paper we give the results of our investigation on the bromination of silicon-containing enynes with different substituents in the enyne system and on the silicon atom.

As examples of the first group of enyne silicohydrocarbons we chose: 1-trimethylsilyl-3-buten-1-yne (I), 1-trimethylsilyl-3-penten-1-yne (II), 1-trimethylsilyl-3-methyl-3-buten-1-yne (III), and 1-trimethylsilylethynyl-1-cyclohexene (IV).

In the second group of silicohydrocarbons we studied 1-triethylsilyl- and 1-triphenylsilyl-3-buten-1-yne (V) and (VI) and we compared the results with the data for compound (I).

The silicohydrocarbons (I), (III), (V), and (VI) were described previously [2,4-6]; (II) and (IV) have been obtained for the first time.

As a result of the addition of bromine to the above enyne silicohydrocarbons we could expect the formation of adducts of the following three types: acetylenic (A), 1,3-diene (B), and allene (C):

$$R_3Si—C\equiv C—CR'Br—CHR''Br \ (A) \qquad R_3Si—CBr=CBr—CR'=CHR'' \ (B)$$
$$R_3Si—CBr=C=CR'—CHR''Br \ (C)$$

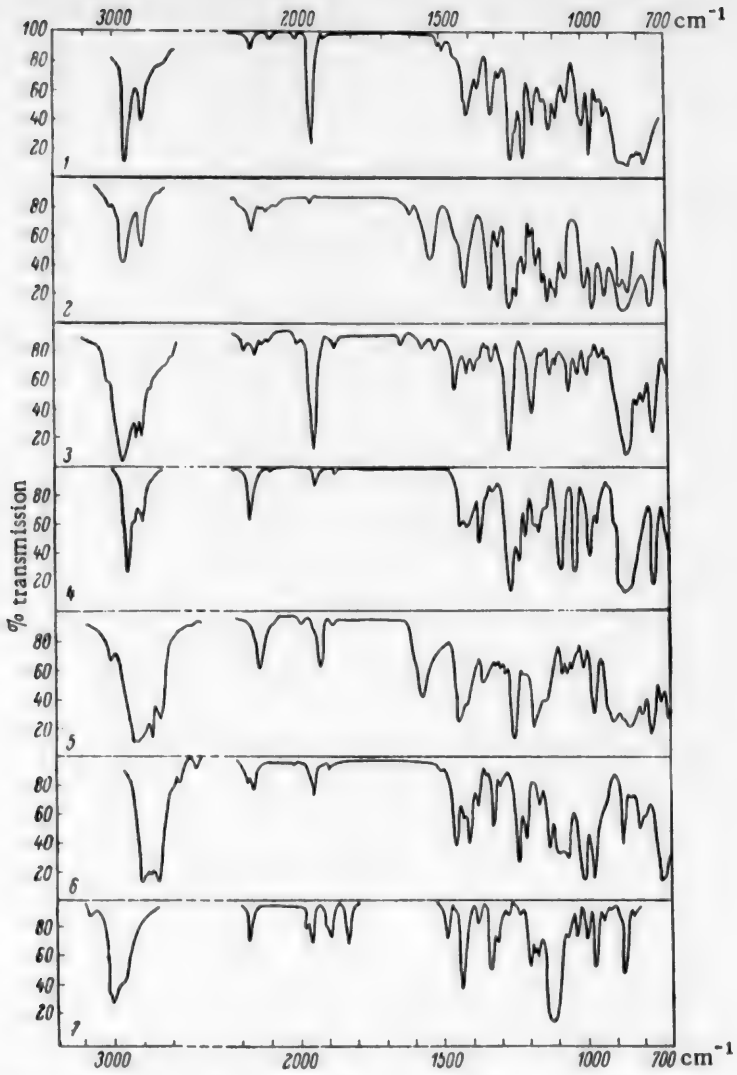
It was previously shown that hydrocarbons of the type of compounds (I), (III), and (V), vinylalkyl acetylenes, add bromine almost exclusively at the double bond [1].

Bromination was carried out in chloroform at −10 to −15°. The starting enyne silicohydrocarbons were taken in 20-25% excess. In most cases the dibromides were easily separated by distillation in a vacuum from the excess starting substances and from the small amount of tetrabromides and other high boiling compounds which were formed.

The structure of the dibromides was shown by study of their infrared spectra and by chemical means.

In the spectrum of the bromination product of trimethylsilylbutenyne (I) (Fig., curve 1) there is an intense band of an allene group (1949 cm^{-1}), a weak band of a triple bond, and a very weak band in the region 1500-1610 cm^{-1}, which is probably due to the presence in small amount of a 1,3-diene dibromide.

*Enyne Compounds. XLVIII.



Infrared transmission spectra of the dibromides (thickness of layer about 30 μ). 1) 1-Trimethylsilyl-3-buten-1-yne; 2) 1-trimethylsilyl-3-buten-1-yne (Expt. b); 3) 1-trimethylsilyl-3-penten-1-yne; 4) 1-trimethylsilyl-3-methyl-3-buten-1-yne; 5) 1-trimethylsilylethynyl-1-cyclohexene; 6) 1-triethylsilyl-3-buten-1-yne; 7) 1-triphenylsilyl-3-buten-1-yne.

Thus it was established that the addition of bromine to trimethylsilylbutenyne (I) occurs almost exclusively in position 1,4 with formation of adduct (C). Side products are the acetylene (A) and possibly the 1,3-diene (B) dibromide.

This conclusion was confirmed by the results on ozonization and dehydrobromination of the substance studied.

With splitting by ozone we obtained bromoacetic and formic acids.

When alcoholic alkali acted on the dibromide in the cold, it gave vinylbromoacetylene. Evidently there was first a hydrolytic splitting of the dibromide with formation of hexamethylsiloxane and vinylacetylene-1,4-dibromide, and then the latter split out hydrogen bromide by the mechanism studied previously [7].

$$(CH_3)_3Si{-}CBr{=}C{=}CH{-}CH_2Br \longrightarrow \begin{matrix} (CH_3)_3Si{-}OH \\ \downarrow \\ [(CH_3)_3Si]_2O \end{matrix} + \begin{matrix} CHBr{=}C{=}CH{-}CH_2Br \\ \downarrow \\ BrC{\equiv}C{-}CH{=}CH_2 \end{matrix}$$

Vinylbromoacetylene was identified by its constants and infrared spectrum.

Bromine added in an analogous way to trimethylsilyl-3-penten-1-yne (II). In the infrared spectrum of the dibromide there was a very strong frequency of the allene group and weak frequencies of the acetylenic and double bonds (Fig., curve 3).

In distinction from the above two, 1-trimethylsilyl-3-methyl-3-buten-1-yne (III) added bromine chiefly at the double bond, that is, in the same way as its hydrocarbon analog. In the infrared spectrum of this dibromide there was an intense band of a triple bond (2182 cm^{-1}) and a weak band for the allene group (1955 cm^{-1}) (Fig., curve 4).

Trimethylsilylethynylcyclohexene (IV), to judge by the spectrum (Fig., curve 5), adds bromine in all three possible ways. In the spectrum there is an intense band of the 1,3-diene group (1563 cm^{-1}), of the acetylene bond (2147 cm^{-1}), and a less intense band for the allene group (1937 cm^{-1}). However, the dibromides in this case were not isolated in a sufficiently pure state and in the distillation there was evolution of hydrogen bromide, and so isomerization was possible.

For an explanation of the influence on the order of addition of bromine of the character of the radicals on the silicon atom, we studied bromination under the same conditions of triethyl- and triphenylsilylbutenynes (V) and (VI).

Triethylsilylbutenyne (V) adds bromine with formation of a mixture of allene and also acetylene dibromides. In comparison with the trimethyl analog (I) there is in the infrared spectrum of the dibromide of (V) less intensity in the allene band and more in the acetylene band. The band in the region 1500-1650 cm^{-1}, which can be assigned to absorption by the 1,3-diene group, is very weak.

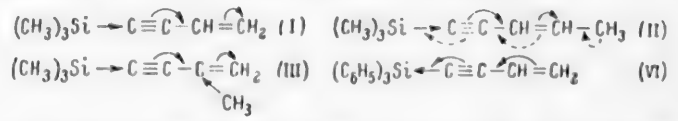
Triphenylsilylbutenyne (VI) behaves in an entirely different way toward bromine. A solution of (VI) in chloroform does not decolorize bromine immediately. On standing in the cold for three days, the bromine is completely absorbed, but the reaction product is then partly tarry. Bromination at 35-40° takes place with evolution of hydrogen bromide and also with tar formation in the reaction mixture. The evolution of hydrogen bromide shows that there is substitutive bromination.

In the infrared spectrum of the bromination product from (VI), in the first stages of the reaction there is no notable change, though bromine is used up. Then, with absorption of bromine, there begins to be a decrease in intensity of the band from the acetylene bond and especially from the vinyl group. Evidently there first occurs mostly a reaction of substitution in the ring, and then at the same time as the substitution reaction there is addition of bromine, chiefly at the double bond.

These results of the experiments on bromination of enyne silicohydrocarbons permit us to consider that the triple bond in these compounds has an increased reactivity as compared to the corresponding hydrocarbons. This is shown by the greater tendency toward 1,4-addition.

The increased activity of the triple bond is probably connected with the deformation of its electron cloud under the influence of the silicon atom (with participation of the d-shell).

The observed change in direction of addition of bromine depending on the position of the methyl group in the enyne chain can be explained on the basis of the usual theory of electron shift.



In the case of compounds (I) and (V), under the influence of a strong inductive effect of the trialkylsilyl group, the greatest activity at the first moment of adding an electrophilic reagent should be found in atom C_4. This agrees with the experimental results. The relatively great percentage of 3,4-addition in case (V) as compared to (I) can be explained by the screening of the first position by the ethyl groups.

In the molecule of the silicohydrocarbon (III) the effect produced by the trimethylsilyl group is strengthened by the action in the same direction of the effect of the methyl group. This perhaps also explains the almost exclusive 3,4-addition of bromine to compound (III).

In the molecule of silicohydrocarbon (II) two substituents act on the enyne system in opposite directions. The chief direction of bromine addition is determined by that substituent which causes the greater shift in the electron shell, that is, the trimethylsilyl radical. The latter, according to the results of Bowden [8], has greater nucleophilic action than does methyl.

In the case of trimethylsilylethynylcyclohexene (IV) there is a complex combined effect determined by the silicon-containing radical and the radical of the ring which leads to formation of a mixture of all possible products.

There is particular interest in the relation of triphenylsilylbutenyne (VI) to bromine. The slight reactivity with respect to electrophilic reagents of the conjugated enyne system here depends on the specific distribution of electron density. The triphenylsilyl group as distinguished from the trialkylsilyls is an electrophilic substituent [9], attracting electrons from the enyne system and passivating it as occurs in the case of esters of vinylacetylene carboxylic acid [10]. At the same time, the reactivity of the methyl nucleus is increased and it reacts easily with bromine. Further addition of bromine at the double bond perhaps occurs by a nucleophilic mechanism. The problem of the behavior of such a system in the addition reaction was discussed previously [10].

Thus it was shown that enyne silicohydrocarbons do not add bromine in the same order as indicated in the literature [2, 3]. We have been able to explain the possible reasons for such a sharp difference in results. In the case of trimethylsilylbutenyne (I) we have established that with slow distillation of the dibromide, especially in the presence of a large amount of tetrabromide, there is isomerization of the allene dibromide into the 1,3-diene, accompanied by slight warming. Such isomerization probably also occurred in the experiments of our predecessors.

The 1,3-dibromide of the silicohydrocarbon (I) was distinguished from the mixture of allene and acetylene dibromides obtained in the bromination of substance (I) by its constants, ozonization products, and infrared spectrum. It has a lower boiling point and on ozonization gave oxalic acid. In the infrared spectrum of the 1,3-diene dibromide there was an intense frequency for a conjugated system of double bonds (1534 cm^{-1}) and two deformation frequencies characteristic for the vinyl group (924 and 998 cm^{-1}). However, it should be noted that isomerization under these conditions is not complete. In the spectrum of the isomerization product there are also frequencies of the starting allene (very weak) and acetylene dibromides.

In order to exclude the possibility of false conclusions, in all cases we determined the structure of the bromination products in small samples in solution without distilling them. For this we compared the infrared spectra of equimolecular solutions in CCl_4 of the starting silanes, and their bromination products at −20° in the ratio of 1 : 1 in the same solvent. The results were compared with the data for the distilled dibromides. Differences occurred only when isomerization occurred during distillation.

Thus, as a result of the investigation it was established that silicon-containing enynes add bromine in a different way than the analogous hydrocarbons.

EXPERIMENTAL

Trimethyl-, triethyl-, and triphenylsilylbutenynes (I), (V), and (VI) were prepared by the action of the corresponding trialkyl or triaryl halosilanes on vinylacetylene magnesium bromide.

1-Trimethylsilyl-3-buten-1-yne (I): b.p. 52-53° (80 mm), d^{20}_4 0.7712, $n^{20}D$ 1.4512.

1-Triethylsilyl-3-buten-1-yne (V), b.p. 74-76° (20 mm), d^{20}_4 0.8145, $n^{20}D$ 1.4695.

The same product, obtained in a yield of 75% from triethyliodosilane and vinylacetylene magnesium bromide, had the constants: b.p. 78° (20 mm), d^{20}_4 0.8111, $n^{20}D$ 1.4712. We assume that this form was purer.

1-Triphenylsilyl-3-buten-1-yne (VI), m.p. 91°.

1-Trimethylsilyl-3-methyl-3-buten-1-yne (III) was obtained by dehydration of dimethyl-trimethylsilylethynyl carbinol over a catalytic amount of $KHSO_4$. B.p. 32-34° (15 mm), d^{20}_4 0.7854, $n^{20}D$ 1.4510.

Silicohydrocarbons (I), (III), (V), and (VI) had constants close to those given for them in the literature [2,4-6, 10, 11].

Preparation of 1-trimethylsilyl-3-penten-1-yne (II). To a cooled (ice-salt mixture) ether solution of 3-penten-1-yne magnesium bromide obtained from 12 g of magnesium, 39 ml of ethyl bromide, and 27.5 g (0.41 g-mole) of 3-penten-1-yne (mixture of cis-trans forms with b.p. 44-46°) was added dropwise with energetic stirring trimethyl-

chlorosilane (48 g). The mixture was stirred for three hours more and left to stand overnight. Then the reaction mixture was heated for two hours on a water bath, and after cooling was decomposed with water. The ether solution of the reaction products was dried over $CaCl_2$. After distillation we obtained 29 g (51% calculated on the hydrocarbon) of enyne silicohydrocarbon (II).

1-Trimethylsilyl-3-penten-1-yne (II):

B.p. 46.5-49° (20 mm), d^{20}_4 0.7811, $n^{20}D$ 1.4600.

Found %: C 69.56, 69.57; H 10.16, 10.18; Si 19.88, 20.01. $C_8H_{14}Si$. Calculated %: C 69.53; H 10.14; Si 20.32.

1-Trimethylsilylethynyl-1-cyclohexene (IV) was obtained by an analogous method from ethynylcyclohexene and trimethylchlorosilane with a yield of 40%.

B.p. 107-108° (20 mm), d^{20}_4 0.8616, $n^{20}D$ 1.4940.

Found %: C 74.16, 74.18; H 10.15, 10.18; Si 15.69, 15.12. $C_{11}H_{18}Si$. Calculated %: C 74.13; H 10.01; Si 15.77.

Bromination of 1-trimethylsilyl-3-buten-1-yne (1).

a) To a solution of 12.4 g (0.1 g-mole) of compound (I) in 50 ml of chloroform with cooling to −15 to −10° and energetic stirring in the course of one hour we added dropwise 11 g (0.07 g mole) of bromine in 25 ml of chloroform. At the end of the reaction the chloroform was distilled off in a low vacuum (water pump) and the residue was fractionated at 5 mm with a Widmer pump. We thus obtained the following fractions: 1st to 90°, 0.7 g; 2nd, 90-91°, 9.3 g (47%); 3rd, 91-101°, 0.7 g; residue (polybromides) 3.3 g.

For the second, the main fraction (chiefly 1-trimethylsilyl-1,4-dibromo-1,2-butadiene):

B.p. 103-104° (10 mm), d^{20}_4 1.4640, $n^{20}D$ 1.5372, MR 58.60; calc. 58.71.

Found %: Br 56.28, 56.83. $C_7H_{12}SiBr_2$. Calculated %: Br 56.33.

Infrared spectrum: 701 s, 755 s, 782 w, 801 w, 840-870 v.s., 921 m, 941 v.w., 976 s, 1001 m, 1064 m, 1101 m, 1123 m, 1146 w, 1176 m, 1211 s, 1256 s, 1303 w, 1331 m, 1276 w, 1414 s, 1512 w, 1603 w, 1949 s, 2018 v.w., 2102, v.w., 2177 w, 2897 s, 2958 v.s. cm^{-1}.

When 4 g of the resulting dibromide was treated with 3.68 g of KOH in 30 ml of methanol at −10 to −5° for four hours, 41.5% of the bromine in the sample of dibromide dissolved. By dilution of the mixture with water we isolated an oil which after washing with a saturated solution of $CaCl_2$ and drying over $CaCl_2$ had $n^{20}D$ 1.5179. The infrared spectrum of this oil practically did not differ from the spectrum of known 1-bromo-1-buten-3-yne obtained according to Carothers and Jacobson [12].

From the products of ozonization of the dibromide (3.9 g) after decomposition of the ozonide with hydrogen peroxide we isolated by extraction with ether: formic acid (b.p. 42-45° at 15 mm, $n^{20}D$ 1.4682; qualitative test with permanganate in the cold is positive), and bromoacetic acid with m.p. 49°.

b) To a solution of 20 g of compound (I) in 100 ml of chloroform we added under the usual conditions an approximately equivalent amount of bromine in 50 ml of chloroform. After distillation of the chloroform the reaction mass was slowly fractionated in a vacuum at 10 mm. During the distillation we observed a slight spontaneous warming. The reaction product (22 g) was collected in the range 80-110° (10 mm). On repeated distillation we obtained the following fractions: 1st to 95°, 2 g; 2nd, 95-96°, 13.5 g (49%); 3rd, 96-100°, 0.8 g; residue 2.5 g.

The fraction 95-96° (10 mm) (chiefly 1-trimethylsilyl-1,2-dibromo-1,3-butadiene):

d^{20}_4 1.4700, $n^{20}D$ 1.5280.

Found %: Br 55.80, 55.71. $C_7H_{12}SiBr_2$. Calculated %: Br 56.33.

Infrared spectrum: 700 s, 759 s, 840-870 v.s., 924 s, 972 s, 998 s, 1063 s, 1094 s, 1108 w, 1126 s, 1146 s, 1164 m, 1184 w, 1206 m, 1231 m, 1253 s, 1298 m, 1326 s, 1414 s, 1534 s, 1607 w, 1960 w, 1977 w, 2173 m, 2898 m, 3082 m, cm^{-1}.

As a result of ozonization of the substance (4 g) we obtained formic acid (identified by qualitative test) and oxalic acid (m.p. 100°).

Bromination of trimethylsilyl-3-penten-1-yne (II). By the action of 6.4 g (0.04 g-mole) of bromine in 10 ml of chloroform on 7 g (0.05 g-mole) of (II) in 40 ml of chloroform under the previously described conditions we obtained 11 g of bromides. On vacuum distillation at 3 mm we obtained the following fractions: 1st to 85°, 2 g; 2nd, 85-87°, 5.2 g (44%); 3rd 87-90°, 1.2 g; residue 2.2 g.

The main fraction (a mixture of 1-trimethylsilyl-1,4-dibromo-1,2-pentadiene and 1-trimethylsilyl-3,4-dibromo-1-pentyne):

B.p. 85.5-86.5° (3 mm), d^{20}_4 1.3930, $n^{20}D$ 1.5342.

Found %: Br 53.18, 53.00. $C_8H_{14}SiBr_2$. Calculated %: Br 53.69.

Infrared spectrum: 698 w, 754 s, 783 s, 806 s, 840 s, 858 s, 912 v.w., 944 w, 973 v.w., 985 m, 991 v.w., 1029 w, 1050 m, 1093 w, 1108 w, 1140 v.w., 1175 s, 1250 s, 1318 w, 1362 v.w., 1380 m, 1408 m, 1447 m, 1517 w, 1567 w, 1639 w, 1870 v.w. 1937 s, 2148 w, 2189 w, 2867 w, 2899 s, 2922 s, 2961 v.s., cm^{-1}.

Bromination of 1-trimethylsilyl-3-methyl-3-buten-1-yne (III). From 7 g (0.05 g-mole) of (III) and 6.4 g (0.04 g-mole) of bromine under the above conditions we obtained 12 g of bromides. On distillation in a vacuum (5 mm) we obtained the following fractions: 1st to 84°, 2 g; 2nd, 84-85°, 5.6 g (47%); 3rd, 85-90°, 1 g; residue 1 g.

The main fraction (chiefly 1-trimethylsilyl-3-methyl-3,4-dibromo-1-butyne):

d^{20}_4 1.3820, $n^{20}D$ 1.5125.

Found %: Br 52.95, 52.35. $C_8H_{14}SiBr_2$. Calculated %: Br 53.69.

Infrared spectrum: 704 m, 764 s, 857 s, 966 w, 982 s, 1038 s, 1090 s, 1143 v.w., 1164 m, 1177 w, 1216 m, 1230 m, 1255 v.s, 1330 v.w., 1353 v.w., 1375 m, 1411 m, 1425 m, 1443 m, 1890 v.w., 1955 w, 2182 s, 1904 m, 2937 v.w., 2964 v.s., cm^{-1}.

Bromination of 1-trimethylsilylethynyl-1-cyclohexene (IV). From 10 g (0.056 g-mole) of (IV) and 7.2 g (0.044 g-mole) of bromine we obtained 17 g of bromides. Distillation in a vacuum at 5 mm gave the following fractions: 1st to 135°, 4 g; 2nd 135-145°, 3 g; 3rd, 145-155°, 4 g; residue 6 g. In the distillation we observed evolution of hydrogen bromide.

On repeated distillation of the 2nd and 3rd fractions we isolated a small fraction. We give its properties below:

B.p. 128-130° (3.5 mm), d^{20}_4 1.3830, $n^{20}D$ 1.5442.

Found %: Br 46.38, 46.02. $C_{11}H_{18}SiB_2$. Calculated %: Br 47.34.

Infrared spectrum: 700 s, 728 s, 761 s, 790 m, 829-890 v.s., 920 v.w., 967 s, 1001 w, 1027 v.w., 1044 w, 1058 w, 1074 w, 1132 m, 1174 s, 1248 v.s., 1343 w, 1410 m, 1432-1443 s, 1565 m, 1634 w, 1675 w, 1937 m, 2147 s, 2164 v.w., 2835 s, 2863 s, 2902 s, 2940 v.s., 3017 w, cm^{-1}.

Bromination of 1-triethylsilyl-3-buten-1-yne (V). From 6.8 g (0.041 g-mole) of (V) and 5.3 g (0.033 g-mole) of bromine we obtained 11.5 g of bromides. The chief fraction (a mixture of 1-triethylsilyl-1,4-dibromo-1,2-butadiene and 1-triethylsilyl-3,4-dibromo-1-butyne; yield 50%):

B.p. 118-120° (4 mm), d^{20}_4 1.3599, $n^{20}D$ 1.5220.

Found %: Br 49.00, 48.91. $C_{10}H_{18}SiBr_2$. Calculated %: Br 49.08.

Infrared spectrum: 740 s, 792 v.w., 807 w, 845 v.w., 864 m, 928 v.w., 975 s, 1006 v.s, 1065 s, 1116 s, 1125 m, 1165 w, 1207 m, 1233 s, 1300 v.w., 1324 m, 1379 w, 1414 s, 1432 v.w., 1461 s, 1510 v.w., 1595 v.w., 1949 m, 2163 m, 2177 w, 2740 v.w., 2810 v.w., 2880 v.s., 2915 s, 2952 v.s., 3040 v.w., cm^{-1}.

Bromination of 1-triphenylsilyl-3-buten-1-yne (VI). Bromination of compound (VI) at 35-40° in CCl_4 with an equivalent amount of bromine gave a solution whose infrared spectrum (with respect to CCl_4) is given below.

Infrared spectrum: 827 w, 865 s, 913 v.w., 941 w, 970 s, 996 m, 1033 m, 1063 w, 1109 v.s., 1164 m, 1174 m, 1190 m, 1225 w, 1266 w, 1305 m, 1327 s, 1376 w, 1430 s, 1487 m, blank, 1835 m, 1894 m, 1964 m, 1980 w, 2178 m, 30.16 s, 30.24 s, 3062 v.s., 3073 s, 31.42 w, cm^{-1}.

Isolation and separation of the products was not successful because of their tarring.

SUMMARY

1. We have investigated the order of addition of bromine to six enyne silicohydrocarbons with different structures.

2. We have shown that in all cases there is addition of bromine in the 1,4-position and at the ethylene bond. The greatest amount of allene 1,4-adduct is given by 1-trimethylsilyl-3-buten-1-yne and the least by 1-trimethylsilyl-3-methyl-3-buten-1-yne.

3. We have showed that the dibromides of 1-trimethylsilyl-3-buten-1-yne can: 1) isomerize when heated, with formation of the 1,3-diene dibromide; 2) split out vinylbromoacetylene under the influence of alcoholic alkali.

4. We have observed that the triphenylsilyl radical, in distinction from the trialkylsilyl radicals, passivates the enyne system. In the bromination of 1-triphenylsilyl-3-buten-1-yne there is substitution of a bromine atom in the ring.

5. We have explained the regularities which we have observed on the basis of the theory of electron shifts.

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INVESTIGATIONS IN THE FIELD OF CONJUGATED SYSTEMS

CXXIX. THE ORDER OF ADDITION OF TERTIARY ALKYL HALIDES TO PROPENYL-, ISOPROPENYL-, AND VINYLMETHYLACETYLENES*

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Tertiary alkyl halides add to vinylacetylene principally at the triple bond with the formation of 1-tert-alkyl-2-halogenobutadienes-1,3. In the case of tertiary alkyl chlorides, allene adducts also are obtained in small amount, but the radical even in this case adds to the end acetylene atom. This order of addition has been demonstrated by the formation of trimethylacetic acid from the adducts of tertiary butyl chloride and bromide to vinylacetylene on oxidation, and by the formation of only 2,2-dimethylhexane on catalytic hydrogenation [1, 2].

At the same time, vinylethylacetylene adds tertiary butyl chloride and bromide with the formation mainly of an aldehyde adduct with the radical on the end ethylene atom of the conjugated system. When these adducts are oxidized, trimethylpropionic acid is produced [3].

In order to determine the mechanism of the effect of alkyl radicals on the order of addition of tertiary alkyl halides to enyne systems, we investigated the addition reactions of tertiary butyl chloride and bromide in the presence of zinc ahlides to the three closest homologs of vinylacetylene of different structure—propenyl-, isopropenyl-, and vinylmethylacetylene.

In the molecule of propenylacetylene the methyl group causes a shift of the electron cloud along the chain of conjugation in the direction of the triple bond [4], which should increase the activity of the latter with respect to the positively polarized tertiary butyl radical in the additive complex, apparently, of the following type: $(CH_3)_3C^+(ZnHal_3)^-$. On the other hand, the methyl group creates steric difficulties, which hinder the addition of the tertiary butyl radical at the site of the double bond. These two factors should favor the formation of adducts (I) or (II) of the six possible ones:

$(CH_3)_3C-CH=CHal-CH=CH-CH_3$ (I)

$(CH_3)_3C-CH=C=CH-CHHal-CH_3$ (II)

$HC\equiv C-CHHal-CH(CH_3)-C(CH_3)_3$ (III)

$CHHal=C=CH-CH(CH_3)-C(CH_3)_3$ (IV)

$CHHal=C(C(CH_3)_3)-CH=CH-CH_3$ (V)

$CH\equiv C-CH(C(CH_3)_3)-CHHal-CH_3$ (VI)

Actually adduct (I) is predominantly obtained with a small admixture of adduct (II).

The frequencies of a terminal acetylene group do not appear in the infrared spectra of the two addition products. Consequently, isomers (III) and (VI) are not formed at all.** The presence in the spectrum of rather intense bands of a conjugated system of double bonds and a deformation band at 940 cm^{-1}, which is characteristic of the group $-CH=CH-$ (Fig. 1, Curves 1 and 2), permits us to reject for the main product all the formulas except (I) and (V).

*Enyne compounds XLIX.

**The band for the valence vibrations of the acetylenic hydrogen is so intense that it permits detection of less than 1% of compounds with a terminal acetylene group.

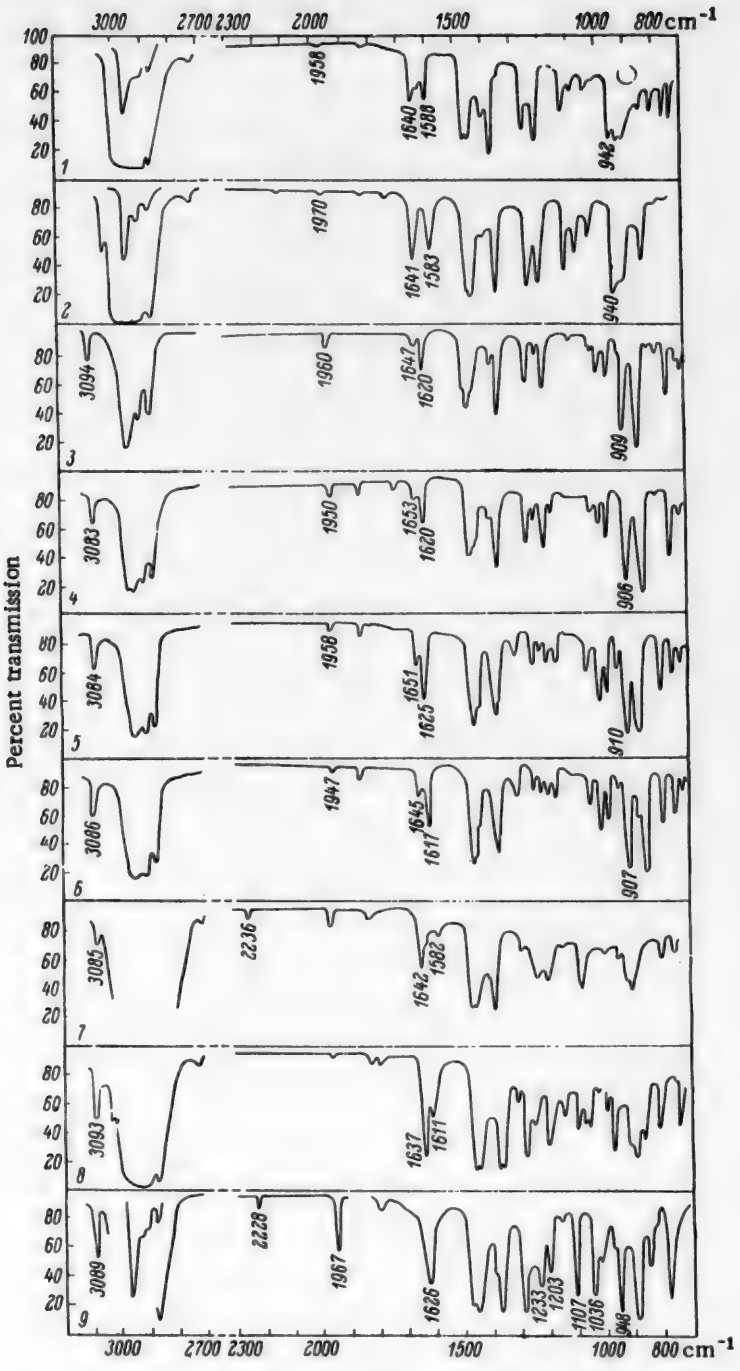

Fig. 1. Infrared transmission spectra of adducts of tertiary alkyl halides to enyne hydrocarbons (thickness of layer 32-36 μ). 1) Propenylacetylene + $(CH_3)_3C-Cl$, 2) propenylacetylene + $(CH_3)_3C-Br$, 3) isopropenylacetylene + $(CH_3)_3C-Cl$, 4) isopropenylacetylene + $(CH_3)_3C-Br$, 5) isopropenylacetylene + $C_2H_5(CH_3)_2C-Cl$, 6) isopropenylacetylene + + $C_2H_5(CH_3)_2C-Br$, 7) vinylmethylacetylene + $(CH_3)_3C-Cl$, 8) vinylmethylacetylene + $(CH_3)_3C-Br$, 9) products of addition of hydrogen bromide to 2,5,5-trimethylhexen-1-yne-3.

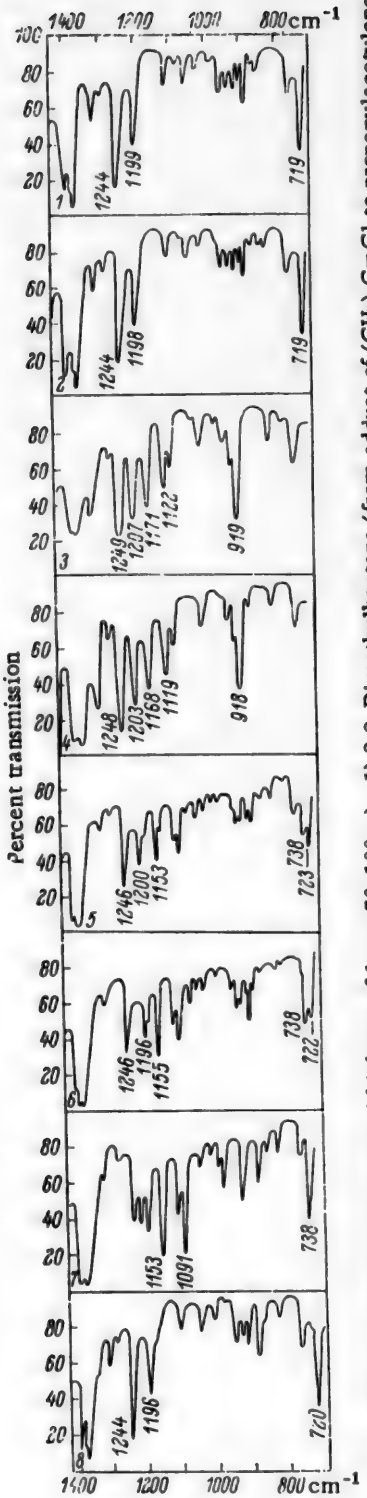

Fig. 2. Infrared transmission spectra (thickness of layer 70-100 μ). 1) 2,2-Dimethylheptane (from adduct of $(CH_3)_3C-Cl$ to propenylacetylene), 2) 2,2-dimethylheptane (from adduct of $(CH_3)_3C-Br$ to propenylacetylene), 3) 2,2,5-trimethylhexane (from adduct of $(CH_3)_3C-Br$ to isopropenylacetylene), 4) known 2,2,5-trimethylhexane, 5) mixture of 2,2-dimethylheptane and 2,2,3-trimethylhexane (from adduct of $(CH_3)_3C-Cl$ to vinylmethylacetylene), 6) mixture of 2,2-dimethylheptane and 2,2,3-trimethylhexane (from adduct of $(CH_3)_3C-Br$ to vinylmethylacetylene), 7) known 2,2,3-trimethylhexane, 8) known 2,2-dimethylheptane.

The choice between these two formulas for the adducts was made on the basis of data from their catalytic hydrogenation. On hydrogenation, only 2,2-dimethylheptane containing no trace of 2,2,3-trimethylhexane, a possible reduction product of adduct (VI),* was obtained from the two adducts. The infrared spectra of the reduction products (Fig. 2, Curves 1 and 2) differ from the spectrum of known 2,2-dimethylheptane only by the presence of a weak frequency at 893 cm^{-1}, which apparently belongs to a nonhydrocarbon contaminant.

Since in the infrared spectra of the starting adducts there are weak frequencies at about 1960 cm^{-1}, it should be assumed that they contain an admixture of allene adducts (II), but not (IV), because on reduction only allenes of the type of (II) can give 1,2-dimethylheptane.

Thus, in the case of propenylacetylene the tertiary butyl radical adds exclusively to the end acetylene carbon atom.

As a result of the addition of the tertiary alkyl halides to isopropenylacetylene (the reaction was carried out with tertiary butyl and amyl chlorides and bromides) we can expect the formation of the following six compounds:

$$R-CH=CHal-\underset{\displaystyle CH_3}{\underset{|}{C}}=CH_2 \quad (Ia)$$

$$R-CH=C=\underset{\displaystyle CH_3}{\underset{|}{C}}-CH_2Hal \quad (IIa)$$

$$HC\equiv C-\underset{\displaystyle CH_3}{\underset{|}{CHal}}-CH_2-R \quad (IIIa)$$

$$CHHal=C=\underset{\displaystyle CH_3}{\underset{|}{C}}-CH_2-R \quad (IVa)$$

$$CHHal=CR-\underset{\displaystyle CH_3}{\underset{|}{C}}=CH_2 \quad (Va)$$

$$HC\equiv C-\underset{\displaystyle CH_3}{\underset{|}{CR}}-CH_2Hal \quad (VIa)$$

In the isopropenylacetylene molecule the methyl radical causes a shift of the electron cloud in the direction of the double bond and at the same time does not create great steric hindrances around the terminal ethylene atom of the conjugated system. Consequently, in this example it could be established whether the electron shifts determine to any extent the order of addition of the halogen derivatives.

Experiments showed that in this case only compounds of formula (Ia) are produced with a very small admixture of adducts of formula (IIa).

In the infrared spectra of all the adducts (Fig. 1, Curves 3-6), there were intense frequencies of a conjugated system of

*2,2,3-Trimethylhexane impurity in 2,2-dimethylheptane is detected with certainty from the frequencies given in Table 2 at a content of more than 5%.

multiple bonds with a terminal isopropenyl group (909, 1620, 3094 cm^{-1}) and a weak frequency of an allene group (1960 cm^{-1}). The frequencies of the acetylenic bond were not detected. Thus, the presence of the isomers (IIIa) and (VIa) was excluded

The choice between formulas (Ia) and (Va) for the 1,3-diene adduct and between (IIa) and (IVa) for the allene adduct impurity was made on the basis of data from the catalytic hydrogenation in the example of the reactions with tertiary butyl chloride and bromide. As a result of hydrogenation we obtained in both cases only 2,2,5-trimethylhexane, which was identical with known 2,2,5-trimethylhexane with respect to its constants and its infrared spectrum.

Thus, it was established that radicals add to the isopropenylacetylene molecule only on the end acetylene carbon atom, i.e., in the same order as to vinyl- and propenylacetylene. Consequently, the electron shifts caused by the methyl radical do not affect the order of addition of the halogen derivatives to the enyne systems studied.

Adducts (Ia) and (IIa) can be prepared also by another method, namely by the addition of hydrogen halides to 2,5,5-trimethylhexen-1-yne-3.

We carried out the reaction of the above named hydrocarbon with hydrogen bromide in the presence of Cu_2Br_2 and isolated the hydrobromide, which differed distinctly with respect to its constants and infrared spectrum from a mixture of (Ia) and (IIa). This hydrobromide had a number of frequencies that were absent from the spectra of compounds (Ia) and (IIa), for example 948, 1107, 2228 cm^{-1}. The frequencies 1203, 1036, 1967 cm^{-1} were considerably more intense (Fig. 1, Curve 9). The presence in the spectrum of the frequencies 2228 and 1967 cm^{-1} undoubtedly indicated a considerable content of the acetylenic (VII) and allenic (IIb) or (VIII) isomers along with the 1,3-diene isomer (Ib). Consequently, the addition of hydrogen bromide to 2,2,5-trimethylhexen-1-yne-3 goes to a considerable extent in the direction of the double bond, with the formation of bromides which cannot be obtained as a result of the addition of tertiary butyl bromide to isopropenylacetylene.

$$(CH_3)_3C-C\equiv C-\underset{\displaystyle CH_3}{\underset{|}{C}}Br-CH_3 \quad (VII) \qquad (CH_3)_3C-CBr=C=\underset{\displaystyle CH_3}{\underset{|}{C}}-CH_3 \quad (VIII)$$

It has previously been shown that the principal direction of addition of hydrogen halides to vinylalkylacetylenes is addition at the triple bond with the formation of adducts of the type of (I) or (II) [5, 6]. Investigation of the infrared spectra of the hydrobromides of vinylethyl- and isopropenylacetylenes, however, showed that they contain small admixtures of the isomers also, which are formed by the participation in the reaction of the double bond [7]. In the case of 2,5,5-trimethylhexen-1-yne-3 this "anomalous" direction of the reaction is expressed to a considerable extent.

Vinylmethylacetylene adds tertiary butyl chloride and bromide with the formation mainly of higher telomers. The yield of simple adducts is extremely small (10-15%).

In contrast to the two isomers of vinylmethylacetylene already considered, it has a triple bond shielded by a radical. The methyl group, as in the case of isopropenylacetylene, causes a shift in electron density in the direction of the double bond. The first factor has a substantial effect on the order of addition of alkyl halides. Vinylmethylacetylene adds tertiary butyl chloride and bromide both at the triple and the double bond. These two groups of adducts are formed in similar amounts.

In the infrared spectra, especially of the adduct of tertiary butyl bromide, the frequencies of the conjugated 1,3-diene grouping are clearly expressed (Fig. 1, Curves 7 and 8). The weak intensity of the frequencies of the allene grouping (about 1960 cm^{-1}) permits us to speak of the presence of the adducts (IIb) or (IVb) only as small impurities. The acetylenic adducts (IIIb) and (VIb) are practically absent, since the materials practically do not absorb in the region 2200-2300 cm^{-1}.

When the chloride is reduced, it yields a mixture of 2,2-dimethylheptane and 2,2,3-trimethylhexane in the ratio 3 : 2, and when the bromide is reduced it yields these compounds in the ratio 2 : 3. Analysis was carried out by selecting concentrations of these two hydrocarbons with a calculation of the intensity of the frequencies recorded in Table 2. The accuracy of the determination was of the order of 2-5%. The infrared spectra of the mixtures of hydrocarbons obtained on reduction are shown in Fig. 2 (Curves 5 and 6). It should be noted that in both spectra there is the frequency 893 cm^{-1}, which does not belong to either of the expected hydrocarbons. Apparently it belongs to a halogen-containing impurity (0.5-1.0% of halogens was found in the hydrocarbons; this impurity could not be removed by distillation over sodium).

TABLE 1. Results of Experiments on the Addition of Tertiary Alkyl Chlorides and Bromides to Enyne Hydrocarbons

Hydrocarbon	Alkyl halide	Reaction time (days)	Yield of adduct (in %)	Residue (in g)	Boiling point (10 mm)	Constants of adducts				Found, %			Empirical formula	Calc., %		
						d_4^{20}	n_D^{20}	MR found	MR calc.	C	H	Cl		C	H	Cl
$HC\equiv C-CH=CH-CH_3$	$(CH_3)_3C-Cl$	7	30	9 *	56—59°	0.9019	1.4742	48.31	47.69	68.48	10.01	21.90, 21.97	$C_9H_{15}Cl$	68.18	9.53	22.35
	$(CH_3)_3C-Br$	5	38	11 *	72—75	1.1305	1.4862	51.58	50.59	—	—	39.04, 39.12	$C_9H_{15}Br$	53.20	7.45	39.36
$HC\equiv C-C(CH_3)=CH_2$	$(CH_3)_3C-Cl$	20	31	5.2 **	47—48	0.8990	1.4596	48.30	47.70	68.42, 68.38	9.92, 9.82	22.34, 22.49	$C_9H_{15}Cl$	68.18	9.53	22.35
	$(CH_3)_3C-Br$	15	28	7.5 **	60—61	1.1202	1.4795	51.44	50.59	53.35, 53.40	7.60, 7.65	39.15, 39.03	$C_9H_{15}Br$	53.20	7.45	39.36
	$(C_2H_5)(CH_3)_2C-Cl$	30	40	6.0 **	62—63.5	0.9027	1.4648	52.87	52.31	69.66, 69.67	9.99, 10.09	20.60, 20.65	$C_{10}H_{17}Cl$	69.55	9.92	20.53
	$(C_2H_5)(CH_3)_2C-Br$	15	38	4.0 **	75—76	1.1146	1.4868	56.01	55.20	55.67, 55.74	7.98, 8.06	36.52, 36.45	$C_{10}H_{17}Br$	55.31	7.90	36.80
$CH_3-C\equiv C-CH=CH_2$	$(CH_3)_3C-Cl$	27	12	25.0 ***	54—57	0.9085	1.4704	48.71	47.70	68.31, 68.54	9.79, 9.72	22.00, 21.97	$C_9H_{15}Cl$	68.18	9.53	22.35
	$(CH_3)_3C-Br$	23	14	31.0 ***	62—67	1.1378	1.4902	51.60	50.59	—	—	39.04, 39.12	$C_9H_{15}Br$	53.20	7.45	39.36

* From 0.2 mole of hydrocarbon.

** From 0.1 mole of hydrocarbon.

*** From 0.3 mole of hydrocarbon.

TABLE 2. Constants of Hydrogenation Products and of Known Hydrocarbons

Hydrocarbon	Boiling point	d_4^{20}	n_D^{20}	H_2 absorbed (in % of calc.)	Characteristic frequencies of infrared spectrum	Remarks
From adduct of $(CH_3)_3C$-Cl to propenylacetylene	131—135°	0.7123	1.4030	82	1244, 1199, 719	
From adduct of $(CH_3)_3C$-Br to propenylacetylene	131—134	0.7128	1.4030	92	1244, 1198, 719	
From adduct of $(CH_3)_3C$-Br to isopropenylacetylene	120—124	0.7071	1.4010	82	1249, 1207, 1171, 1122, 919	
From adduct of $(CH_3)_3C$-Cl to vinylmethylacetylene	129—134	0.7216	1.4072	90	1246, 1200, 1153, 738, 723	
From adduct of $(CH_3)_3C$-Br to vinylmethylacetylene	130—134	0.7240	1.4092	86	1246, 1196, 1155, 738, 722	
2,2-Dimethylheptane	131—132	0.7084	1.4022	— —	1244, 1196, 790	Our data
	130.4	0.7105	1.4024			[18]
	134—134.5	0.7292	1.4105	— —	1153, 1091, 738	Our data
2,2,3-Trimethylhexane	133.6	0.7292	1.4105			[18]
	121—122	0.7075	1.4010	— —	1248, 1213, 1168, 1119, 918	Our data
2,2,5-Trimethylheptane	121—123	0.7091	1.3997			[18]

The ratio found between the two directions of addition of the halogen derivatives to vinylmethylacetylene, in this case to a greater extent than in the others previously considered, probably does not reflect the actual ratio, since the main process in this case is a more extensive telomerization. Usually the greatest tendency to extensive telomerization is shown by primary halogen derivatives [8, 9], and therefore it may be assumed that the adduct (IIb) is formed as the main compound, but at the moment of cessation of the reaction it is able to react to a considerable extent with other molecules of the hydrocarbon. For all the rest of the possible adducts active telomerization is not probable.

Thus as a result of this investigation it has been established that the triple bond is considerably more reactive with respect to the addition of alkyl halides, probably in the form of the complexes $R^+ZnHal_3^-$, than the double bond. This apparently is associated with its higher polarizability. The carbonium ions, like H^+ ions (in the addition of hydrogen halides) [5, 6] or HgX^+ ions (in the Kucherov reaction) [10] and in contrast to anionoid particles (in the addition reactions of lithium alkyls [11], lithium amides [12], diazo compounds [13], nitrile oxides [14], and also of free radicals in combination replacement reactions with diazonium salts [15]) always attack predominantly or exclusively the acetylenic bond. The polarizing effect of the radicals does not affect the order of addition. Steric hindrances, however, may partially change the order of addition, as happens in the case of vinylmethylacetylene in reaction with alkyl halides and in the case of propenylacetylene in reaction with diazo compounds. Apparently in reactions which go selectively at the acetylenic bond π-complexes appear as intermediate products. For the case of the addition of alkyl halides such complexes will have the following form.

EXPERIMENTAL

Addition of tertiary alkyl halides. A mixture of 0.1-0.3 mole of hydrocarbon (+ 0.1 g of hydroquinone), an equivalent amount of alkyl halide, and 1.5-3 g of zinc halides was shaken

at room temperature with interruptions at night for a period of several days. Then the catalyst was bound with diethylamine and the mixture was filtered through a glass filter and distilled in vacuum. The results of the experiments are given in Table 1.

Reduction of adducts. About 0.03 mole of adduct in 50 ml of methanol was hydrogenated in the presence of 8 g of Pd/$CaCO_3$ until absorption of hydrogen ceased. Usually 82-92% of the calculated amount of hydrogen was used.

The reaction products were steam-distilled off and salted out from the distillate with a saturated solution of $CaCl_2$, dried over $CaCl_2$, and distilled with a small Widmer column.

The constants of the saturated hydrocarbons obtained are given in Table 2, and the infrared spectra in Fig. 2.

Synthesis of saturated hydrocarbons with known structure. a) 2,2-Dimethylheptane was prepared by the scheme:

$$(CH_3)_3C-C\equiv CMgBr \xrightarrow{CH_2=CH-CH_2Br} (CH_3)_3C-C\equiv C-CH_2-CH=CH_2 \xrightarrow{H_2} \rightarrow (CH_3)_3C-C_5H_{11}$$

To an ether suspension of tert-butylacetylenylmagnesium bromide prepared from 0.4 mole of tert-butylacetylene, was added with slight external cooling and mechanical stirring 10 g of Cu_2Br_2, and then 0.35 mole of freshly distilled allyl bromide was added dropwise. During this process the liquid separated into two layers. After six hours heating on a water bath the mixture was treated with dilute hydrochloric acid. The ether layer was separated, washed with sodium carbonate solution, dried over $CaCl_2$, and distilled.

Twenty-five and eight tenths grams (60%) of allyl-tert-butylacetylene was obtained.

B.p. 68° (100 mm), d^{20}_4 0.7581, $n^{20}D$ 1.4312, MR 41.70; calc. 41.29.

Found %: C 88.45, 88.60; H 11.83, 11.79. C_9H_{14}. Calculated %: C 88.52; H 11.56.

IR-spectra (principal frequencies): 913 v.s., 988 v.s., 1204 v.s., 1262 v.s., 1295 s., 1361 v.s., 1414 s, 1454 s, 1477 s, 1641 v.s., 2237 w, 2284 w, 2874 v.s., 2982 v.s., 3091 s, cm^{-1}.

When 5.42 g of allyl-tert-butylacetylene in 40 ml of methanol was hydrogenated over 4 g of Pd/$CaCO_3$ for 2 hr, 99% of the calculated amount of hydrogen was absorbed. Four grams (83%) of 2,2-dimethylheptane was obtained with the constants given in Table 2 and with the infrared spectrum depicted in Fig. 2 (Curve 8).

b) 2,2,3-Trimethylhexane was prepared by the following scheme:

$$(CH_3)_3C-CO-CH_3 \xrightarrow{C_3H_7MgBr} \rightarrow (CH_3)_3C-\underset{\displaystyle CH_3}{\underset{|}{C}}OH-C_3H_7 \xrightarrow{-H_2O} (CH_3)_3C-\underset{\displaystyle CH_3}{\underset{|}{C}}=CH-C_2H_5 \xrightarrow{H_2} \rightarrow (CH_3)_3C-\underset{\displaystyle CH_3}{\underset{|}{CH}}-C_3H_7$$

To an ether solution of propylmagnesium bromide prepared from 1 mole of magnesium, with mechanical stirring and cooling, was added 90 g of pinacoline in one and a half times its volume of ether. After standing for a day, the magnesium complex was decomposed with dilute hydrochloric acid. The ether layer was washed with a solution of sodium carbonate, dried over $MgSO_4$, and distilled. Twenty-two grams (17%) of 2,2,3-trimethylhexanol-3 was obtained.

B.p. 68-73° (16 mm), d^{20}_4 0.8460, $n^{20}D$ 1.4382, corresponding to the literature data [6].

Twelve grams of alcohol was slowly distilled over 4 g of anhydrous oxalic acid. The hydrocarbon layer of the distillate was dried over $CaCl_2$ and redistilled. Seven and three tenths grams (70%) of hydrocarbons was obtained (obviously a mixture of 2,2,3-trimethylhexene-3 and 2,2-dimethyl-3-propylbutene-3) with b.p. 126-133° and $n^{20}D$ 1.4262.

By hydrogenation of these hydrocarbons in 30 ml of methanol over 3 g of Pd/$CaCO_3$ (97% of the calculated amount of H_2 was absorbed), 2,2,3-trimethylhexane was obtained with the constants given in Table 2 and the infrared spectrum shown in Fig. 2 (Curve 7).

c) 2,2,5-Trimethylhexane was prepared by the following scheme:

$$(CH_3)_3C-C\equiv C-MgBr \xrightarrow{CH_3COCH_3} (CH_3)_3C-C\equiv C-C(OH)(CH_3)_2 \xrightarrow{-H_2O}$$
$$\rightarrow (CH_3)_3C-C\equiv C-\underset{\displaystyle CH_3}{\underset{|}{C}}=CH_2 \xrightarrow{H_2} (CH_3)_3C-CH_2-CH_2-CH(CH_3)_2$$

From tert-butylacetylenylmagnesium bromide and acetone there was prepared in 50% yield the crystalline alcohol 2,2,5-trimethylhexyn-3-ol-2 which has been described in the literature [17].

To a mixture of acetic anhydride and 0.5 ml of orthophosphoric acid heated to 150-160° was slowly added drop by drop a solution of the alcohol in acetic anhydride (total amount of acetic anhydride 4 moles per mole of the alcohol), and the low boiling products were simultaneously distilled off (temperature in the vapors up to 125°). The distillate was neutralized with sodium carbonate, the hydrocarbon was separated, washed with water, and purified from the contaminating carbonyl compounds by heating (for 3 hr) and then distillation with phenylhydrazine with subsequent washing with 5% sulfuric acid.

2,2,5-Trimethylhexen-1-yne-3 (yield 43%).

B.p. 60.5-61° (100 mm), d^{20}_4 0.7473, $n^{20}D$ 1.4420, MR 43.26; calc. 41.85.

Infrared spectrum (principal frequencies): 887 v.s., 1206 s, 1242 s, 1302 v.s., 1364 v.s., 1430 v.s., 1453 v.s., 1474 v.s, 1613 v.s., 2223 v.s., 2974 v.s., 3102 s, cm^{-1}.

When 2.54 g of the hydrocarbon was hydrogenated in 25 ml of methanol over 2 g of Pd/$CaCO_3$, 96% of the calculated amount of H_2 was absorbed. In this process 2,2,5-trimethylhexane was obtained with the constants given in Table 1 and the infrared spectrum shown in Fig. 2, (Curve 4).

Addition of hydrogen bromide to 2,2,5-trimethylhexen-1-yne-3. To a solution of 3 g of Cu_2Br_2 in 5 ml of hydrobromic acid (d 1.7) was added 3 g of the hydrocarbon and the mixture was vigorously shaken for 7 hr. Then the oily layer was separated off, washed with water, dried, and distilled in vacuum at 10 mm. In this process the following fractions were obtained: 1st up to 58°, 0.35 g; 2nd 58-70°, 2.1 g; residue 0.8 g.

Redistillation yielded a product boiling at about 60° (10 mm), d^{20}_4 1.1377, $n^{20}D$ 1.4860.

Found %: Br 39.89, 39.72. $C_9H_{15}Br$. Calculated %: Br 39.36.

The infrared spectrum of the compound is given in Fig. 1 (Curve 9).

SUMMARY

1. The order of addition of tertiary alkyl halides to the three closest possible homologs of vinylacetylene—penten-3-yne-1, 2-methylbuten-1-yne-3, and penten-2-yne-3—has been investigated.

2. It has been shown that the first two hydrocarbons add alkyl halides in such a manner that the radical is joined to the end acetylene atom of the conjugated system, and predominantly diene halogen derivatives are formed with a small admixture of allenes.

3. In contrast to the first two homologs, penten-1-yne-3 adds alkyl halides with fixation of the radical both on the end ethylenic and the first acetylenic carbon atoms. In this process also predominantly diene halogen derivatives are formed with a small admixture of allenes.

4. On the basis of the experimental data obtained it has been concluded that the electron shifts in the molecules of the hydrocarbons investigated apparently do not affect the order of addition of alkyl halides. The triple bond proved to be the more reactive. Steric hindrances, however, may lead to partial addition at the ethylene bond.

5. It has been shown that as a result of addition of hydrogen bromide to 2,5,5-trimethylhexen-1-yne-3 in the presence of Cu_2Br_2, a bromide is obtained which is not identical with the adduct of tertiary butyl bromide to isopropenylacetylene.

6. In the process of synthesis of the known saturated hydrocarbons for evidence of the structure of the adducts of the tertiary halogen derivatives, two enyne hydrocarbons were prepared for the first time: allyl-tert-butylacetylene and isopropenyl-tert-butylacetylene.

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All abbreviations of periodicals in the above bibliography are letter-by-letter transliterations of the abbreviations as given in the original Russian journal. *Some or all of this periodical literature may well be available in English translation.* A complete list of the cover-to-cover English translations appears at the back of this issue.

INVESTIGATIONS IN THE FIELD OF CONJUGATED SYSTEMS

CXXX. ARYLHALOGENATION OF VINYLACETYLENE BY PHENYL-, p-TOLYL-, m- AND p-CHLOROPHENYL-, AND p-ANISYLDIAZONIUM SALTS*

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In an investigation of the arylchlorination of vinylacetylene by diazonium salts A. V. Dombrovskii established the formation of 1-aryl-2-chlorobutynes-3 [1]. An investigation of the infrared spectra and some of the chemical properties of the reaction products of vinylacetylene and phenyldiazonium chloride undertaken in our laboratory led to the conclusion that the reaction follows at least two directions: the formation of the chlorophenylbutyne (I) isolated by A. V. Dombrovskii and, apparently, of 1-chloro-4-phenylbutadiene-1,2 (II) [2]).

$C_6H_5—CH_2—CHCl—C\equiv CH$ (I) $C_6H_5—CH_2—CH=C=CHCl$ (II)

The structure of the phenylchlorobutyne was confirmed by direct determination of the end acetylene group, by conversion to 1-phenylbuten-1-yne-3, and by hydrogenation to phenylbutane [1, 2]. In favor of the formula given above for the allene chloride (II) are its hydrogenation in a mixture with chlorophenylbutyne to phenylbutane and data on its dehydrohalogenation: the compound proved to be stable toward a solution of KOH in dioxane.

Continuing our study of the arylhalogenation of vinylacetylene, we tried to confirm the structure of the allene chloride (II) by ozonization and oxidation with potassium permanganate of a mixture of the chlorides (I) and (II). Instead of the expected phenylacetic acid, however, benzoic acid was obtained in both cases. The latter compound could be formed either as a result of more extensive oxidation of chlorides (I) and (II) or as a result of oxidation of other isomeric chlorides present in the products of phenylchlorination of vinylacetylene in small amounts, for example, (III) and (IV).

$C_6H_5—CH=C=CH—CH_2Cl$ (III) $C_6H_5—CH=CCl—CH=CH_2$ (IV)

The first hypothesis seems to us the more probable, since on ozonization and oxidation we did not isolate either chloroacetic or oxalic acid. Also the formula (III) for the allene chloride does not conform with the data on the effect of KOH on the allene chloride: the chlorine was found to be highly stable.

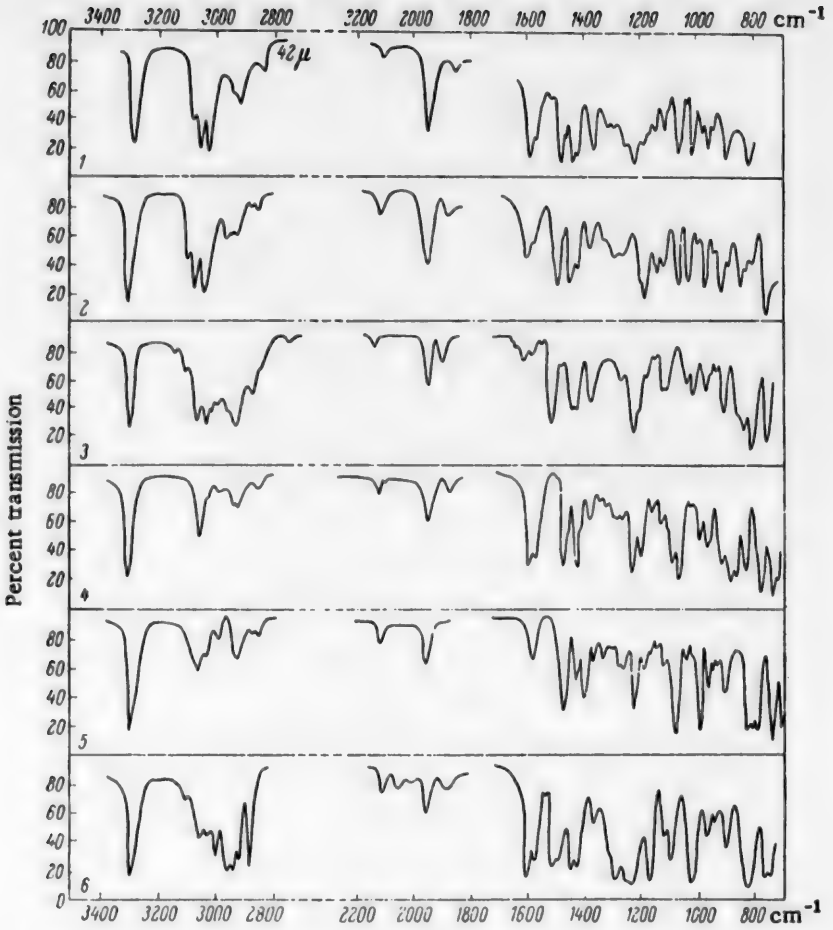
We further considered it necessary to determine whether the arylchlorination and the arylbromination of vinylacetylene with phenyldiazonium salts follow the same route. For this purpose we carried out the reaction of vinylacetylene with phenyldiazonium bromide.

We were not able to determine the acetylene bromide content in the resulting mixture by the usual method [3], apparently because the reagent split out hydrogen bromide from the compound to be analyzed. The infrared spectrum of the mixture of bromides that was obtained, however, indicated definitely that it did not differ essentially in composition from the mixture of (I) and (II) usually obtained on arylchlorination (Figure, Curves 1 and 2).

Consequently the formation of the allene adduct along with the acetylenic one takes place also in the arylbromination of vinylacetylene.

Finally, we tried to establish any connection between the distribution of the electron density in the benzene ring of the aryldiazonium compound and the direction of the arylhalogenation. For this purpose we carried out the

*Enyne Compounds L.



IR transmission spectra (thickness of layer about 30 μ) of products of arylhalogenation of vinylacetylene with diazonium salts. 1) Phenyldiazonium chloride; 2) phenyldiazonium bromide; 3) p-tolyldiazonium chloride; 4) m-chlorophenyldiazonium chloride; 5) p-chlorophenyldiazonium chloride; 6) p-anisyldiazonium chloride.

reaction of vinylacetylene under the same conditions suggested by A. V. Dombrovskii with phenyl-, p-tolyl-, m- and p-chlorophenyl-, and p-anisyldiazonium chlorides.*

In the products of all these reactions we determined the acetylenic adduct content and compared the intensities of the frequencies of the acetylene bond and the allene group in their infrared spectra (Figure, Curves 1, 3-6).

As a result, we established that in all cases the two products, the acetylenic and the allene adducts, were obtained, and in ratios which were reproducible in replicate experiments. In the infrared spectra of all the products of arylchlorination there were the frequencies of the end acetylene (3300 and 2110 cm^{-1}) and the allene (1950 cm^{-1}) groups.

The formation of the acetylenic adduct is facilitated by substituents which increase the electrophilic nature of the aryl radical by an inductive mechanism (Cl, OCH_3). The greatest relative yield of the acetylenic adduct was obtained from the reaction of vinylacetylene with p-chlorophenyldiazonium chloride and the smallest from the reaction with p-tolyldiazonium chloride. The chlorine atom in the para position has a stronger favorable effect on the yield of the acetylenic adduct than the same atom in the meta position.

*A. V. Dombrovskii [1] had previously carried out the reactions with phenyl-, p-chlorophenyl-, and p-anisyldiazonium chlorides.

Constants, Composition, and Yields of Products of Arylhalogenation of Vinylacetylene

Diazonium salt	Empirical formula	Constants of adduct: boiling point (pressure in mm)	d_4^{20}	n_D^{20}	Found (%): C	Found (%): H	Found (%): Hlg	Calc. (%): C	Calc. (%): H	Calc. (%): Hal	Yield of acetylenic adduct (in %)	Total yield (in %)
$C_6H_5N_2Cl$	$C_{10}H_9Cl$											
Our data		82—83° (2)	1.0798	1.5643	—	—	—	—	—	—	53.0, 52.6	33
		92—93 (5)	1.0780	1.5649	—	—	—	—	—	—	47.4, 47.5	37.4
Data of A. V. Bombrovskii [1]		105 (?) (3)	1.0788	1.5641	—	—	—	—	—	—	—	46
$C_6H_5N_2Br$	$C_{10}H_9Br$	88—90 (2)	1.3424	1.5865	57.31, 57.39	4.36, 4.48	38.32, 38.31	57.42	4.31	38.28	—	46
		96—98 (4)	1.3448	1.5872	—	—	—	—	—	—	—	34
CH_3-$C_6H_4N_2Cl$	$C_{11}H_{11}Cl$	93—93.5 (3)	1.0559	1.5589	74.13, 74.37	6.26, 6.15	19.75, 19.80	73.97	6.16	19.87	57.6, 58.1	40
		93—94 (3)	1.0549	1.5590	—	—	—	—	—	—	53.8, 52.8	36
m-Cl-$C_6H_4N_2Cl$	$C_{10}H_8Cl_2$	98—100 (2)	1.2072	1.5758	60.36, 60.52	4.16, 4.18	35.45, 35.70	60.33	4.03	35.70	68.1, 69.0	29
		103—104 (3)	1.2076	1.5755	—	—	—	—	—	—	70.6, 71.8	32
p-Cl-$C_6H_4N_2Cl$	$C_{10}H_8Cl_2$											
Our data		105—106 (2)	1.2090	1.5732	—	—	—	—	—	—	89.0, 88.1	27
Data of A. V. Dombrovskii		107 (2)	1.2056	1.5737	—	—	—	—	—	—	—	23
p-CH_3O-$C_6H_4N_2Cl$	$C_{11}H_{11}OCl$											
Our data		112—113 (2)	1.1280	1.5680	—	—	—	—	—	—	74.0	10.5
		112—113 (2)	1.1267	1.5668	—	—	—	—	—	—	73.1	9.8
Data of A. V. Dombrovskii		118 (2)	1.1263	1.5675	—	—	—	—	—	—	74.9, 76.0	20

The total yield of arylchlorination products was greatest from the reaction with p-tolyldiazonium chloride and worst from the reaction with p-anisyldiazonium chloride.

It was interesting to compare the data obtained on the effect of the structure of the diazonium salts on the order of arylchlorination with data on the stability and reactivity of the diazonium salts used in other reactions [4]. We were not able to discover any strict parallel between the activity of the diazonium compounds in azo coupling reactions or in the formation of phenols and the direction of the arylchlorination; in general, however, the more reactive diazonium salts gave a greater yield of acetylenic adducts.

The absence of a definite relationship probably is associated with the fact that all the reactions were carried out under the same conditions, which were not the most favorable for each of the diazonium compounds in the sense of the position of the acid-base equilibrium.

EXPERIMENTAL

The arylchlorination was carried out in acetone solution in the presence of $CuCl_2$ exactly as prescribed by A. V. Dombrovskii. The vinylacetylene was passed into the reaction mixture after the addition of all the diazonium solution over the course of 2 hr.

The phenylbromination of vinylacetylene (25 g) was carried out also in acetone solution with a neutral solution of phenyldiazonium bromide prepared by the diazotization of 31 g of aniline in 120 ml of 40% hydrobromic acid in the presence of 14.5 g of $CuBr_2$.

The results of the experiments are compared in the table.

The infrared spectra were determined with an IKS-14 spectrograph.

Ozonization and oxidation of products of phenylchlorination of vinylacetylene. a) Four and three tenths grams of the compound in 35 ml of methylene chloride was saturated with ozone for 5.5 hr. The ozonides were decomposed with hydrogen peroxide. From the acidified solution, formic acid (b.p. 35° at 50 mm, $n^{20}D$ 1.3689; positive calomel test) and benzoic acid (m.p. 121°; mixed melting point 121°) were extracted with ether.

b) Powdered potassium permanganate (8 g) was added in small portions to a vigorously stirred mixture of 5.9 g of the products of phenylchlorination of vinylacetylene and 12 g of magnesium sulfate in 50 ml of water until a violet color appeared in a sample that was withdrawn. Then sulfur dioxide gas was passed into the solution until the manganese dioxide dissolved, and after acidification with sulfuric acid the organic acids were extracted with ether in an extractor. In the residue after removal of the ether only benzoic acid was found.

SUMMARY

1. It has been shown that on arylhalogenation [of vinylacetylene] with phenyl-, p-tolyl-, m- and p-chlorophenyl-, and p-anisyldiazonium salts acetylenic and allenic arylhalogenation products are formed.

2. The yields and the ratios between the acetylenic and the allenic adducts depend on the nature and the position of the substituents in the benzene ring.

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All abbreviations of periodicals in the above bibliography are letter-by-letter transliterations of the abbreviations as given in the original Russian journal. *Some or all of this periodical literature may well be available in English translation.* A complete list of the cover-to-cover English translations appears at the back of this issue.

INVESTIGATIONS IN THE FIELD OF CONJUGATED SYSTEMS

CXXXI. PREPARATION OF "SESQUITERPENE" CHLORIDES BY TELOMERIZATION OF PIPERYLENE, ISOPRENE AND CHLOROPRENE WITH DIPIPERYLENE HYDROCHLORIDE (2-CHLORO-6-METHYLNONADIENE) AND CONVERSION OF THEM TO "SESQUITERPENE ALCOHOLS"*

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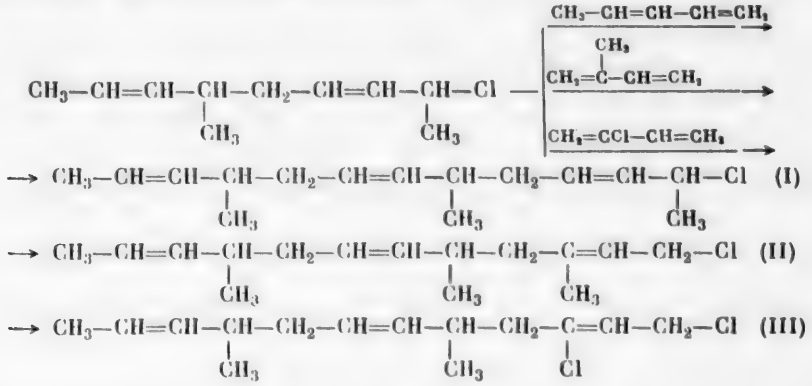
As a result of the telomerization of diene hydrocarbons with their hydrochlorides, mixtures of unsaturated chlorides with the general formula $H-(C_nH_{2n-2})_x-Cl$ are obtained [1-8]. Up to the present time the structure almost exclusively of the primary products of telomerization with x = 2 (the "terpene fraction") has been studied. Some chemical transformations of these products also have been described: hydrolysis [3], reaction with amines [9], with the sodium derivative of acetoacetic ester [10], reaction with urotropine as described by Sommle [11-13], and others.

With respect to the isolation and the transformations of the "sesquiterpene" chlorides (x = 3) there are very few data in the literature. Only some of the properties of the telomer of this type from divinyl with crotyl chloride are known. The corresponding aldehyde was obtained from it by Sommle's reaction [6].

In the present work we have studied the "sesquiterpene" chlorides, tripiperylene hydrochloride (I), dipiperylene-isopropene hydrochloride (II), and dipiperylene-chloroprene hydrochloride (III), which are formed by the telomerization of piperylene, isoprene, and chloroprene with dipiperylene hydrochloride, the telomerization product of piperylene with its hydrochloride (2-chloro-6-methylnonadiene-3,7).



Furthermore, a method has been developed for the isolation of the "sesquiterpene" chlorides from the products of telomerization of the diene hydrocarbons with their hydrochlorides. Direct distillation in vacuum (below 2 mm) of the residue after distilling off the monomers and the "terpene" fraction from the telomerization products is impossible because of the severe decomposition with the evolution of HCl. If, however, a solution of this residue in petroleum ether is passed through a weakly adsorbing silica gel, then it is freed of unstable products and can be subjected to distillation in vacuum in order to isolate the "sesquiterpene" fraction without significant decomposition.

*Diene composition. LXXVIII.

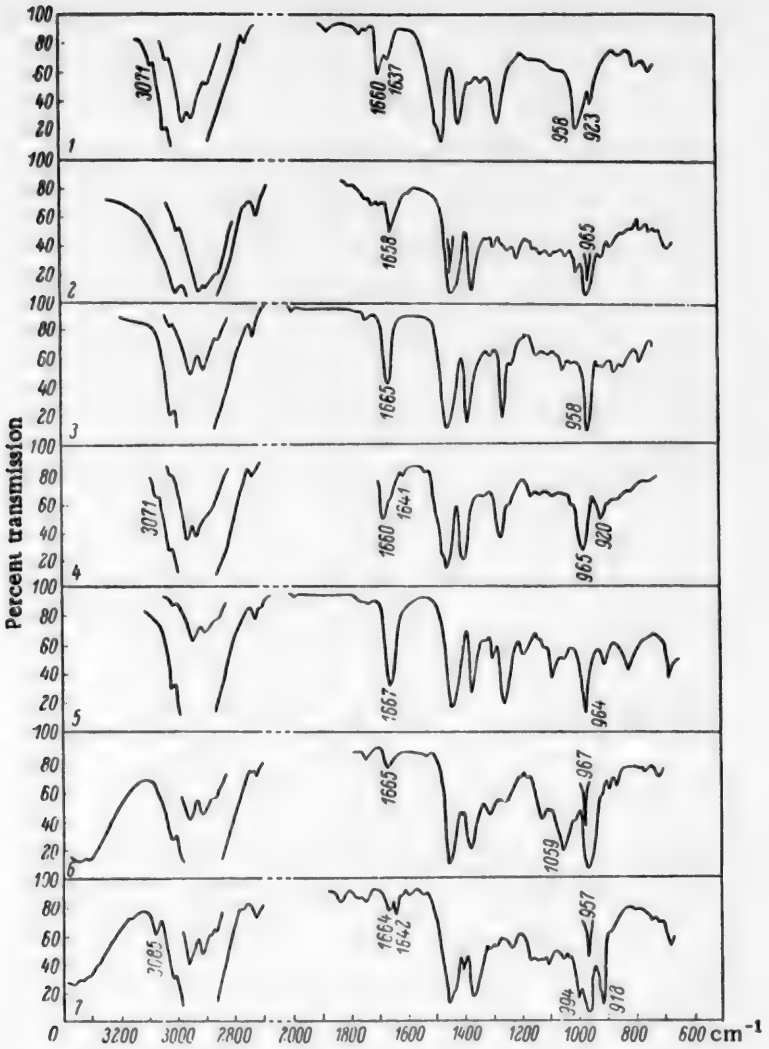


Fig. 1. IR transmission spectra of chlorides and alcohols (thickness of layer 37 mμ). 1) Piperylene-didivinyl hydrochloride; 2) tripiperylene hydrochloride; 3) dipiperylene-isoprene hydrochloride; 4) piperylene-diisoprene hydrochloride; 5) dipiperylene-chloroprene hydrochloride; 6) 6, 10-dimethyltridecatrien-2,7,11-ol-2; 7) 3,6,10-trimethyldodecatrien-1,6,10-ol-3 with admixed 3,6,10-trimethyldodecatrien 3,6,10-ol-1.

The activity of the silica gel is of essential significance in the process of purification. On active silica gel the resinification and dehydrochlorination of the telomers takes place. Silica gel of low activity does not permit carrying out the purification. The experimentally established optimum activity of the silica gel was of the order of 2.2-2.7 ml/g.

In this way the "sesquiterpene" chlorides piperylene-didivinyl hydrochloride (IV), piperylene-diisoprene hydrochloride (V), and tripiperylene hydrochloride (I) were separated from the mixture of telomers of divinyl, isoprene, and piperylene with piperylene hydrochloride.*

* The formulas given for (I)-(V) relate to the main component part of the telomers under consideration.

$$CH_3-CH=CH-\underset{\underset{CH_3}{|}}{CH}-CH_2-CH=CH-CH_2-CH_2-CH=CH-CH_2Cl \quad (IV)$$

$$CH_3-CH=CH-\underset{\underset{CH_3}{|}}{CH}-CH_2-\underset{\underset{CH_3}{|}}{C}=CH-CH_2-CH_2-\underset{\underset{CH_3}{|}}{C}=CH-CH_2Cl \quad (V)$$

The proposed structure for the main part of all the "sesquiterpene" chlorides (I)-(V) was substantiated by their infrared spectra. These spectra had the same characteristics as the spectra of the corresponding terpene chlorides, the structure of which was substantiated by chemical methods.

In the infrared spectra of the chlorides (I)-(III) (Fig. 1), there was only one frequency of the valence vibrations of the double bond (about 1660 cm^{-1}) and in the region 900-1000 cm^{-1} there was only one intense frequency of the deformed CH vibrations in the group $-CH=CH-$ (965 cm^{-1}) and bands which might be ascribed to the vinyl group were absent. The characteristic band of the valence CH vibrations in the $CH_2=$ group (3080 cm^{-1}) also was absent.

In the infrared spectra of the chlorides (IV) and (V) along with the frequencies of the $-CH=CH-$ group there are present also weaker frequencies of the vinyl group (1640, 3070 cm^{-1}). In the region 900-1000 cm^{-1} the deformation frequency of the vinyl group (980 cm^{-1}) does not appear.

In all the chlorides the amount of primary chlorides was determined by the usual method [13]. For compound (I) it amounted to a total of 3-5% (error of the determination). For compounds (II) and (III) it was of the order of 70-80%. These data confirm the formulas (I-III) for the main part of the corresponding telomers. The missing 20-30% possibly represents cyclic isomers. It also is possible that telomers somehow are changed in the process of the determination and do not give a complex with urotropine in 100% yield. In chlorides (IV) and (V) we found 50-60% of primary chlorides, which agrees with the previously considered spectral data.

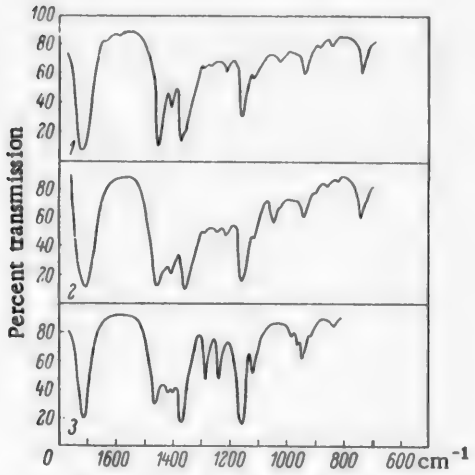
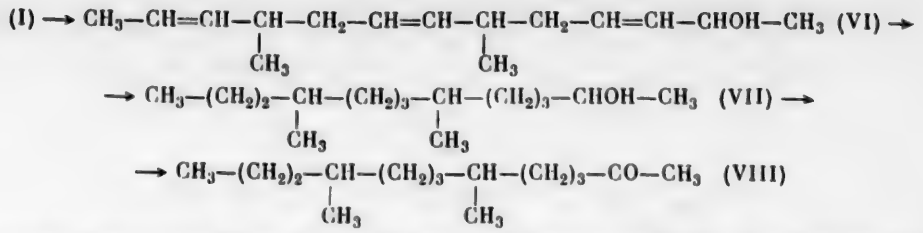


Fig. 2. IR transmission spectra (thickness of layer 37 mμ). 1) 6,10-Dimethyltridecanone-2; 2) 6-methylnonanone-2; 3) 4-methylpentanone-2.

We subjected the chlorides that were isolated to hydrolysis by a known method [3] in order to obtain the "sesquiterpene" alcohols, isomers or analogs of farnesol or nerolidol.

By hydrolysis of chloride (I) we obtained a secondary alcohol (VI), which was a colorless oil with a weak odor reminiscent of nerolidol. In its infrared spectrum, as in that of the starting chloride, there was the frequency of deformed CH vibrations in $-CH=CH-$ group (967 cm^{-1}). The usual frequencies at 1059 and about 3350 cm^{-1} corresponded to the vibrations of the secondary hydroxyl group.

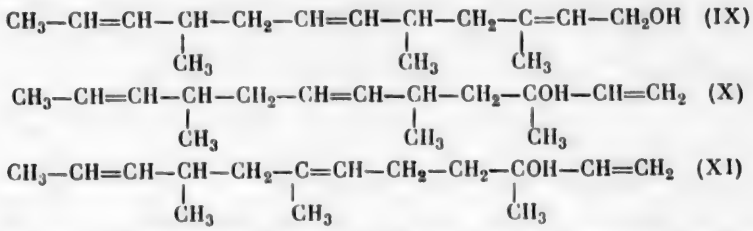
The alcohol (VI) was converted by catalytic hydrogenation to the saturated alcohol (VII) (3 molecules of hydrogen were absorbed per molecule of alcohol). By oxidation of (VII), the ketone (VIII) was obtained, which was almost identical with respect to the number and position of the absorption maxima in its infrared spectrum with the ketone produced by the oxidation of the saturated secondary alcohol obtained by the hydrolysis of the starting 2-chloro-6-methylnonadiene-3,7. In the spectrum of both ketones there is an intense band at 1162 cm^{-1}, which is characteristic of methyl ketones [14]. Consequently, when the "terpene" and "sesquiterpene" chlorides obtained from piperylene are hydrolyzed, secondary alcohols are formed with the hydroxyl group on the second carbon atom, i.e., without an allyl group. The presence of an admixture of the secondary allyl isomer with the hydroxyl on the fourth carbon atom is not very probable, since in the region 1000-1200 cm^{-1} the infrared spectra of both ketones are similar to the spectra of other methyl ketones, for example methyl isobutyl ketone (Fig. 2, Curves 1-3). Ketones with longer radicals have a different type of spectrum in this region [14].



By hydrolysis of the chloride (II) we obtained a mixture of the primary (IX) (30%) and tertiary (X) (70%) alcohols. The primary alcohol content was determined by the phthalation method. This mixture was a colorless liquid with an odor reminiscent of nerolidol. In its infrared spectrum there were intense frequencies of the vinyl group (3085, 1642, and 918 cm^{-1}) along with frequencies of the $-CH=CH-$ group (3025, 1664, and 966 cm^{-1}) (Fig. 1, Curve 5).

We did not succeed in obtaining an alcohol from the chloride (III) under the conditions that we used.

The alcohols (VI) (tripiperylene hydrate), (IX), and (X) (dipiperylene-isoprene hydrates) were isomeric tertiary alcohols, obtained by us previously by Ruzicka's scheme from the "terpene" chlorides which were produced by the telomerization of isoprene with the hydrochlorides of isoprene and piperylene–nerolidol and piperylene-diisoprene hydrate (XI) [15].



The alcohols (VI), (IX), and (X) described in this work differ from the previously investigated alcohol (XI) by their higher boiling point and less pleasant odor. As the isoprene groups are replaced by piperylene groups, the specific gravities and refractive indices decrease and the odor becomes worse.

EXPERIMENTAL

1. Preparation of dipiperylene hydrochloride and tripiperylene hydrochloride. a) To a solution of 2.2 moles of piperylene and 2 moles of its hydrochloride in 70 ml of methylene chloride was added 3 ml of an 11% solution of stannic chloride in dichloroethane and the mixture was stirred at 10° until the specific gravity increased by 0.065 (extent of conversion 58%). Then the telomerization was stopped by adding 0.5 ml of pyridine and the reaction products were distilled in vacuum. One hundred and twenty-five grams of dipiperylene hydrochloride (64% of the total telomers) and 32 g of tripiperylene hydrochloride (16% of the total telomers) were obtained.

b) To a mixture of 0.5 mole of piperylene and 0.5 mole of dipiperylene hydrochloride at 0° was added 1.5 ml of an 11% solution of stannic chloride in dichloroethane. The mixture was stirred until the specific gravity increased by 0.05, during which the temperature of the reaction was kept at about 25° by external cooling. The reaction was stopped by adding 0.5 ml of pyridine. By distillation of the reaction mixture in vacuum (3 mm) 12 g of tripiperylene hydrochloride and 9 g of higher boiling residue were obtained.

c) Twenty grams of the dark residue after distillation of dipiperylene hydrochloride was dissolved in 20 ml of petroleum ether and passed through a column with 30 g of silica gel.* By vacuum distillation at 2 mm 10 g of tripiperylene hydrochloride (53% of the amount of the fraction used) and 6.5 g of higher boiling products were obtained.

* The silica gel for the purification was prepared in the following way. The fraction of ASK silica gel passing through a 65 mesh sieve and held on a 150 mesh sieve, after 3 hr boiling with concentrated hydrochloric acid, washing with water, and treatment with 30% hydrogen peroxide was dried at 120-130° for 5 hr. The activity of the silica gel prepared in this way was 4-6 ml/g (by the benzene-heptane method) [16]. After deactivation with water (15 g per 100 g of silica gel) the activity fell to 2-3 ml/g. A column 10 mm in diameter and 400 mm high, with a lower stopcock, was filled with the silica gel. The filling was carried out by the wet method. Petroleum ether with b.p. 58-60° was used as the eluant. The process was checked by means of the change in refractive index. The rate of passage was 2-3 drops per second. It was entirely possible to work with regenerated silica gel freed of tar by treatment with permanganate solution and then with sodium bisulfite.

Constants of "Sesquiterpene" Telomers and Some of Their Derivatives

Compound	Empirical formula	Boiling point (pressure in mm)	d_4^{20}	n_D^{20}	MR		Found (%)			Calc. (%)		
					found	calc.	C	H	Cl	C	H	Cl
1-Chloro-9-methyldodecatriene-2,6,10 (piperylene-didivinyl hydrochloride (IV)	$C_{13}H_{21}Cl$	102—105° (3)	0.9254	1.4800	65.21	65.70	73.67, 73.97	10.30, 10.42	16.77, 16.76	73.41	9.88	16.71
2-Chloro-6,10-dimethyltrideca-triene-3,7,11 (tripiperylene hydrochloride) (I)	$C_{15}H_{25}Cl$	112—114 (3)	0.9115	1.4842	75.61	74.94	73.98, 73.92	10.57, 10.45	14.41, 14.63	74.82	10.46	14.72
1-Chloro-3,4,9-trimethyldodeca-triene-2,6,10 (dipiperyleneisoprene hydrochloride (II)	$C_{15}H_{25}Cl$	110—114 (3)	0.9069	1.4822	75.80	74.94	74.83, 74.97	10.45, 10.47	14.24, 14.31	74.82	10.46	14.72
1-Chloro-3,7,9-trimethyldodeca-triene-2,6,10 (piperylenediisoprene hydrochloride) (V)	$C_{15}H_{25}Cl$	115—120 (3)	0.9135	1.4898	76.19	74.94	77.43, 77.11	10.89, 10.99	12.12, 12.19	74.82	10.46	14.72
1,3-Dichloro-5,9-dimethyldodeca-triene-2,6,10 (dipiperylene-chloroprene hydrochloride) (III)	$C_{14}H_{22}Cl_2$	119—121 (3)	0.9965	1.4902	75.93	75.19	65.48, 65.45	8.68, 8.78	25.55, 25.43	64.48	8.48	27.05
6,10-Dimethyltridecatrien-3,7,11-ol-2 (VI)	$C_{15}H_{26}O$	142—143 (10)	0.8662	1.4730	72.02	71.59	80.76, 80.37	11.90, 11.72	—	81.02	11.78	—
3,5,9-Trimethyldodecatrien-3,6-10-ol-3 (X) with admixture of 3,5,9-trimethyldodecatrien-3,6,10-ol-1 (IX)	$C_{15}H_{26}O$	134—136 (10)	0.8678	1.4718	71.74	71.59	80.23, 80.37.	11.68, 11.72	—	81.02	11.78	—
6,10-Dimethyltridecanol-2 (VII)	$C_{15}H_{32}O$	144—145 (10)	0.8882	1.4472	72.83	72.99	79.02, 78.93	14.17, 14.09	—	78.88	14.13	—
6,10-Dimethyltridecanone-2 (VIII)	$C_{15}H_{30}O$	133—134 (10)	0.8443	1.4430	71.11	71.48	79.78, 79.80	13.42, 13.43	—	79.86	13.35	—

The constants and analytical data for the tripiperylene hydrochloride (I) as well as for the products described below are given in the table.

Hydrolysis of tripiperylene hydrochloride. To a mixture of 25 ml of a 25% aqueous solution of lead nitrate and 25 g of lead carbonate in 100 ml of acetone heated to boiling was added with mechanical stirring a solution of 40 g of tripiperylene hydrochloride in 40 ml of acetone. The mixture was heated for 14 hr. Then the acetone was distilled off and the reaction products were salted out with NaCl and distilled in vacuum.

From the ether extract was isolated 30 g of unpurified alcohol. Purification was carried out through the boric ester. To the compound obtained was added 20 ml of tributyl borate and the mixture was slowly distilled in vacuum up to 120° (3 mm). The residue was saponified by heating with sodium carbonate solution. The purified alcohol was extracted with ether and distilled in vacuum.

Eleven grams (30%) of tripiperylene hydrate (VI) were obtained with the constants given in the table.

Hydrogenation of tripiperylene hydrate (VI). Three and nine hundredths grams of the alcohol (VI) in 15 ml of methanol was hydrogenated on 3 g of Pd/ $CaCO_3$ with electrolytic hydrogen. In 5 hr 955.5 ml of H_2 was absorbed (749 mm, 20°), which corresponds to 98%. The methanol was distilled off at ordinary pressure and the hydrogenation product was distilled in vacuum. Two and two tenths grams (71%) of 6,10-dimethyltridecanol-2 (VII) was obtained.

Oxidation of dimethyltridecanol (VII). To a solution of 1 g of sodium bichromate in 1.3 g of sulfuric acid and 4.4 ml of water (Kiliani mixture) was added dropwise, with mechanical stirring, 2 g of dimethyltridecanol. To complete the reaction the mixture was heated to 40° for 40 min, during which the black mass which precipitated at first was converted to a clear oily layer. The reaction product was extracted with ether. One and two tenths grams of 6,10-dimethyldecanone-2 (VIII) was obtained.

2. Telomerization of isoprene with dipiperylene hydrochloride. To a stirred mixture of 33 g of isoprene and 80 g of dipiperylene hydrochloride at 0° was added 2 ml of catalyst. In 15 min the temperature reached 25°. It was maintained by external cooling at this level until the specific gravity increased by 0.058, after which the reaction was stopped by the addition of pyridine. By vacuum distillation of the reaction mixture 17.5 g (39.5% of the total amount of telomers) of dipiperylene-isoprene hydrochloride with b.p. 108-118° (3 mm) and 25 g of residue were obtained. By repeated distillation of the compound 12.5 g of product was obtained with the constants given in the table.

The primary chloride content in it was 75%.

Hydrolysis of dipiperylene-isoprene hydrochloride (II). From 10 g of dipiperylene-isoprene hydrochloride was obtained, under the conditions described above, 2.2 g of purified dipiperylene-isoprene hydrate (IX + X) with the constants given in the table.

By the phthalation method 29.7 and 32.3% of primary alcohol was found in the two alcohols.

3. Telomerization of chloroprene with dipiperylene hydrochloride. To a mixture of 42 g of chloroprene and 82 g of dipiperylene hydrochloride at 15° was added 3 ml of catalyst. Stirring at a temperature of 25° was continued until the specific gravity increased by 0.025, after which the reaction practically ceased. We were not able to increase the rate by the addition of new portions of catalyst. The reaction mixture was further treated in the usual way.

Eight grams (35% of total amount of telomer) of dipiperylene-chloroprene hydrochloride with b.p. 115-140° (2 mm) and 15 g of residue were obtained. By repeated distillation of the compound 5.5 g of product was obtained with the constants given in the table.

The primary chloride content was 78%.

4. Preparation of dipiperylene hydrate, its hydrogenation, and oxidation of the hydrogenation products. Hydrolysis of the dipiperylene hydrochloride and purification of the alcohols obtained were carried out in the usual way. 6-Methylnonadien-3,7-ol-2 was obtained. The compound will be described in another communication.

By exhaustive hydrogenation of 6-methylnonadien-3,7-ol-2 over Pd/ $CaCO_3$ 6-methylnonanol-2 was obtained.

B.p. 96-97.5° (12 mm), d^{20}_4 0.8332, $n^{20}D$ 1.4408, MR 50.15; calc. 49.90.

By oxidation of the 6-methylnonanol-2 with Kiliani mixture 6-methylnonanone-2 was obtained.

B.p. 84-84.5° (10 mm), d^{20}_4 0.8384, $n^{20}D$ 1.4300, MR 48.16; calc. 48.39.

Found %: C 77.02, 77.10; H 12.62, 12.73. $C_{10}H_{20}O$. Calculated %: C 76.86; H 12.91.

2,4-Dinitrohydrazone: m.p. 52-52.5° (from alcohol).

Found %: N 16.73, 16.65. $C_{16}H_{24}O_4N_4$. Calculated %: N 16.66.

5. Isolation of piperylene-didivinyl hydrochloride. Twenty grams of the residue after distillation of the terpene fraction from the products of telomerization of divinyl with piperylene hydrochloride was dissolved in 20 ml of petroleum ether and passed through a column with 35 g of silica gel. Nine and two tenths grams (46% of the residue used) of "sesquiterpene" chlorides and 7.2 g of higher boiling products were obtained. By repeated distillation 6.8 g of material was obtained with the constants given in the table. The primary chloride content was 58%.

6. Isolation of piperylene-diisoprene hydrochloride. Twenty-five grams of tarry residue after the terpene fraction had been distilled off from the products of telomerization of isoprene with piperylene hydrochloride was dissolved in 25 ml of petroleum ether and passed through a column with 35 g of silica gel. As a result of distillation 7.2 g of "sesquiterpene" chlorides (29% of the residue used) and 10 g of higher boiling products were obtained. After repeated distillation of the "sesquiterpene" fraction a product was obtained with the constants given in the table. The primary chloride content was 48%. Judged by the analytical data, the compound contained an admixture of hydrocarbons formed as a result of the splitting out of hydrogen chloride on distillation of the "terpene" fraction.

SUMMARY

1. The telomerization reaction of piperylene, isoprene, and chloroprene with dipiperylene hydrochloride (2-chloro-6-methylnonadiene-3,7) has been investigated.

2. Tripiperylene, dipiperylene-isoprene, and dipiperylene-chloroprene hydrochlorides have been prepared and characterized.

3. From the two first hydrochlorides the corresponding "sesquiterpene" alcohols have been prepared.

4. By hydrogenation of the "sesquiterpene" alcohol from piperylene, 6,10-dimethyltridecanol-2 was prepared and by oxidation of the latter 6,10-dimethyltridecanone-2 was obtained.

5. A method has been developed for isolation of the "sesquiterpene" chlorides from the products of telomerization of divinyl, isoprene, and piperylene with piperylene hydrochloride.

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THE SYNTHESIS OF THE ETHYL ESTER OF α-(β'-CARBOXYETHYL)-β-METHYL LEVULINIC ACID

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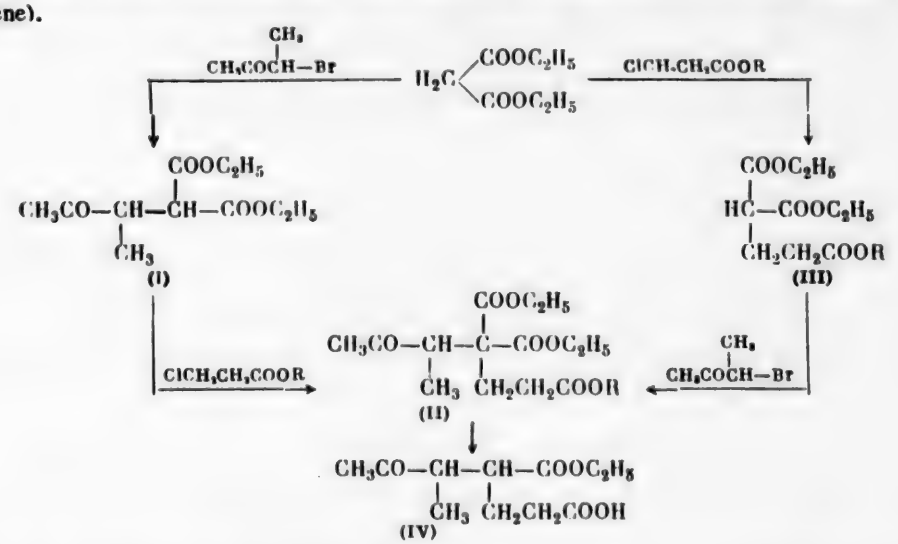
In continuation of our investigation of the Claisen condensation of levulinic [1, 2] and β-methyl levulinic [3, 4] acids it became interesting to study also the esters of α,β-substituted levulinic acids. For this purpose we undertook the synthesis of ethyl α-(β'-carboxyethyl)-β-methyl levulinate. We tried two experimental methods of synthesis, consisting in successive introduction into a molecule of malonic ester of two alkyl radicals with later saponification. The alkylation reactions were carried out with the use of metallic sodium in inert solvents (ether, benzene, xylene).



In the first case, malonic ester as its sodium derivative reacted with α-bromoethyl methyl ketone with formation of the ethyl ester of α-carbethoxy-β-methyl levulinic acid (I). The sodium derivative of compound (I) in the reaction with the methyl or butyl ester of β-chloropropionic acid gave the ethyl ester of α-carbethoxy-α-(β'-carbalkoxyethyl)-β-methyl levulinic acid (II, R = CH_3, C_4H_9) with yields of 4-4.5%. Best results were obtained by changing the order of addition of the alkyl radicals. First the radical of the ester of β-chloropropionic acid was introduced into the malonic ester. The resulting diethyl ester of β-carbalkoxyethylmalonic acid (III, R = CH_3, C_4H_9) reacted with α-bromoethyl methyl ketone giving substance (II) with a yield of 20-24%. Hydrolysis of ester (II) with the calculated amount of sodium alcoholate and water followed by decarboxylation led to ethyl α-(β'-carboxyethyl)-β-methyl levulinate (IV). Simultaneously with ester (IV) there were also formed other hydrolysis products, so that the yield of compound (IV) could be considerably increased.

EXPERIMENTAL

Ethyl ester of α-carbethoxy-2-methyl levulinic acid (I). It was obtained by the method of Adams [5] with a yield of 72%. B.p. 116-118° (2 mm).

Diethyl ester of β-carbomethoxyethyl malonic acid (III, R = CH_3). It was obtained by reaction of sodium malonic ester with methyl β-chloropropionate [6] with a yield of 61.5%.

B.p. 118-120° (2 mm), d^{20}_4 1.116, $n^{20}D$ 1.4415, MR_D 58.25; calc. 57.96.

Diethyl ester of β-carbobutoxyethyl malonic acid (III, R = C_4H_9). To sodium malonic ester obtained from 80 g of malonic ester and 11.2 g of finely divided sodium in 400 ml of absolute ether was added 82.3 g of butyl β-chloropropionate and the mixture was heated for 24 hr. The precipitate was dissolved in 75 ml of water and the substance formed was extracted with 300 ml of ether. After drying over sodium sulfate, the solvent was removed and the residue was distilled. Yield 64.4 g (44.2%).

B.p. 135-136° (3 mm), d^{20}_4 1.0520, $n^{20}D$ 1.4380, MR_D 71.9; calc. 71.84.

Found %: C 58.54, 58.24; H 8.48, 8.55. $C_{14}H_{24}O_6$. Calculated %: C 58.30; H 8.39.

Ethyl ester of α-carboethoxy-α-(β'-carbomethoxyethyl)-β-methyl levulinic acid (II, R = CH_3). To the sodium derivative of β-carbomethoxyethyl malonic ester (III, R = CH_3) obtained from 1.87 g of finely divided sodium and 20 g of β-carbomethoxyethyl malonic ester with 35 ml of anhydrous xylene was added 12.3 g of β-bromoethyl methyl ketone and the mixture was heated for 22 hr at 120°. After cooling it, we added 20 ml of water. The xylene layer was separated and the substance was extracted from the water with 100 ml of ether. From the combined extracts after drying with sodium sulfate we distilled off the solvent. The residue was distilled. Yield 6.4 g (24%).

B.p. 163-165° (2.5 mm), d^{20}_4 1.1630, $n^{20}D$ 1.4851, MR_D 77.64; calc. 76.44 (for the ketone form), 77.49 (for the enol form).

Found %: C 56.93, 56.88; H 7.41, 7.37. $C_{15}H_{24}O_7$. Calculated %: C 56.96; H 7.65.

Ethyl ester of α-carboethoxy-α-(β'-carbobutoxyethyl)-β-methyl levulinic acid (II, R = C_4H_9). a) We added 5.75 g of α-bromoethyl methyl ketone to the sodium derivative obtained from 10 g of β-carbobutoxyethyl malonic ester and 0.88 g of sodium in 40 ml of ether and heated on a water bath for 15 hr. After the usual treatment we isolated the ethyl ester of α-carboethoxy-α-(β'-carbobutoxyethyl)-β-methyl levulinic acid. Yield 2.58 g (20.5%).

B.p. 177-180° (3 mm), d^{20}_4 1.055, $n^{20}D$ 1.4459, MR_D 90.44; calc. 90.27 (for the ketone form), 91.46 (for the enol form).

Found %: C 60.77, 60.32; H 8.69, 8.43. $C_{18}H_{30}O_7$. Calculated %: C 60.33; H 8.43.

b) To the sodium derivative obtained from 1 g of sodium and 10 g of the ethyl ester of α-carboethoxy-β-methyl levulinic acid in 35 ml of anhydrous xylene we added 7.35 g of butyl ester of β-chloropropionic acid and heated for 24 hr. Yield 0.65 g (4.17%). B.p. 177-179° (3 mm).

Ethyl ester of α-(β'-carboxyethyl)-β-methyl levulinic acid (IV). To sodium alcoholate obtained from 0.82 g of sodium and 20 ml of anhydrous alcohol we added 11.2 g of ethyl ester of α-carboethoxy-α-(β'-carbomethoxyethyl)-β-methyl levulinic acid and 0.57 ml of water. On the next day the mixture was boiled for one hour. The excess alcohol was distilled off, the residue was dissolved in 40 ml of water and the substance was extracted with 100 ml of ether. The water layer was acidified with hydrochloric acid (to Congo) and was extracted with 150 ml of ether. After drying with sodium sulfate, the solvent was distilled off and the residue was distilled. Yield 0.4 g (4.5%). B.p. 106-107° (3 mm).

Found %: C 57.60; H 7.60. $C_{11}H_{18}O_5$. Calculated %: C 57.36; H 7.87.

SUMMARY

1. We have carried out the synthesis of α-(β'-carboxyethyl)-β-methyl levulinic acid.

2. In introducing into malonic ester the radicals of α-bromoethyl methyl ketone and esters of β-chloropropionic acid, the yield of dialkylated derivative depends on the order of introduction of the alkyl radicals. The radical of the esters of β-chloropropionic acid should be introduced as the first step of the alkylation.

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THE SYNTHESIS OF THE ETHYL ESTER OF α-METHYL-β-(β'-CARBOXYETHYL)-LEVULINIC ACID

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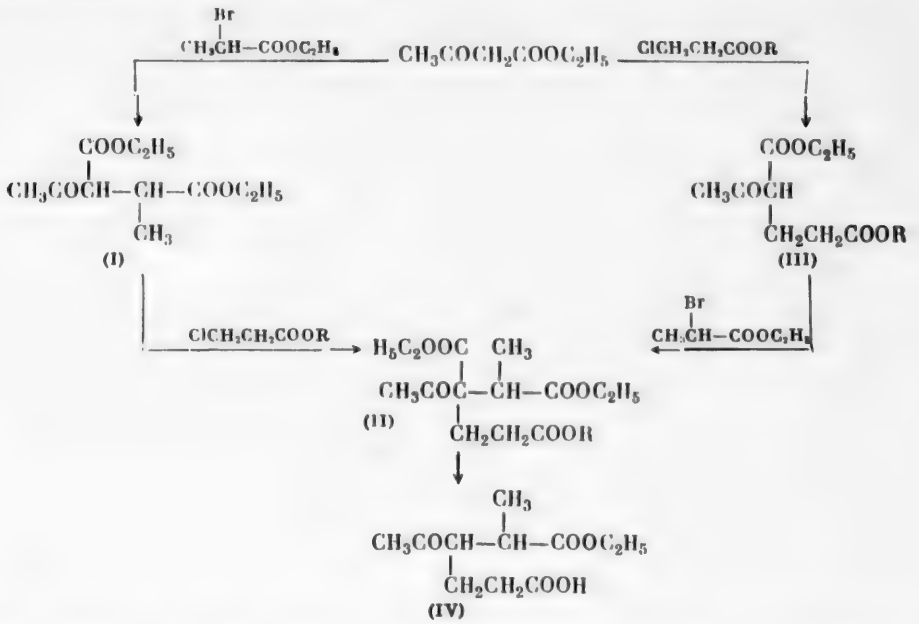
In the previous communication we described the synthesis of the ethyl ester of α-(β'-carboxyethyl)-β-methyl levulinic acid [1]. In order to study the effect of the nature and position of the substituents in levulinic acid esters on their properties we carried out the synthesis of the isomeric compound, ethyl α-methyl-β-(β'-carboxyethyl)-levulinate. In preparing this compound we used successive alkylations of acetoacetic ester by the radicals of α-bromopropionic and β-chloropropionic esters. Here also we found it better to introduce the radical of β-chloropropionic ester in the first step of the alkylation.



In the reaction of the sodium derivative of ethyl acetoacetate with ethyl α-bromopropionate we obtained ethyl α-methyl-β-carbethoxylevulinic acid (I). Its sodium derivative reacted with β-chloropropionic esters with formation of ethyl α-methyl-β-(β'-carbalkoxyethyl)-β-carbethoxylevulinate (II, R = CH_3, C_4H_9). Yield 5.1%. When the order of alkylation is changed, and we first obtain ethyl β-carbalkoxyethylacetoacetate (III, R = CH_3, C_4H_9) and then by reaction with ethyl α-bromoacetate we obtain ester (II), the yield is 36-44.5%. Alkylation with butyl β-chloropropionate under comparable conditions takes place with a somewhat lower yield than with the methyl ester. By saponification of ester (II) with dilute hydrochloric acid we obtain, along with other products, ethyl α-methyl-β-(β'-carboxyethyl)-levulinate (IV).

EXPERIMENTAL

Ethyl α-methyl-β-carbethoxylevulinate (I). Obtained with a yield of 64.9% by [2].

B.p. 126-126.5° (7 mm), d^{20}_4 1.0660, $n^{20}D$ 1.4396, MR_D 56.79; calc. 56.32 (for the ketone form), 77.49 (for the enol form).

Found %: C 56.66, 56.53; H 7.49, 7.54. $C_{11}H_{18}O_5$. Calculated %: C 56.96; H 7.65.

Ethyl β-carbomethoxyethylacetoacetate (III, R = CH_3). To sodium acetoacetic ester obtained from 15.9 g of sodium and 90 g of acetoacetic ester in 450 ml of absolute ether we added 84.05 g of methyl β-chloropropionate and heated on a water bath for 20 hr. Fifty ml of water was added to the reaction mass. The resulting substance was extracted with 300 ml of ether. After drying with sodium sulfate, the solvent was removed and the residue was distilled. Yield 77.1 g (51.0%).

B.p. 124-125° (3.5 mm), d^{20}_4 1.1040, $n^{20}D$ 1.4428, MR_D 51.93; calc. 51.69 (for the ketone form), 52.74 (for the enol form).

Found %: C 55.34, 55.48; H 7.42, 7.21. $C_{10}H_{16}O_5$. Calculated %: C 55.54; H 7.45.

Ethyl β-carbobutoxyethylacetoacetate (III, R = C_4H_9). Forty g of butyl β-chloropropionate was added to sodium acetoacetic ester obtained from 5.6 g of sodium and 31.6 g of acetoacetic ester in 250 ml of absolute ether, and the mixture was heated on a water bath for 16 hr. Forty ml of water was added to the reaction mass. The ether layer was separated and the substance was further extracted from the water layer with 100 ml of ether. After drying with sodium sulfate, the solvent was removed and the residue distilled. Yield 28.4 g (50.8%).

B.p. 130-133° (2 mm), d^{20}_4 1.040, $n^{20}D$ 1.4434, MR_D 65.85; calc. 65.55 (for the ketone form), 66.6 (for the enol form).

Found %: C 60.61, 60.50; H 8.56, 8.60. $C_{13}H_{22}O_5$. Calculated %: C 60.43; H 8.58.

Ethyl α-methyl-β-(β'-carbomethoxyethyl)-β-carbethoxylevulinate (II, R = CH_3). To the sodium derivative obtained from 77.1 g of ethyl β-carbomethoxyethylacetoacetate (III, R = CH_3) and 8.2 g of sodium in 350 ml of xylene we added 65 g of ethyl α-bromopropionate. The reaction mass was heated with stirring at 120° for 20 hr. After cooling, we added 100 ml of water. The xylene layer was separated and the substance was extracted from the water with 300 ml of ether. From the combined extracts after drying with sodium sulfate we distilled off the solvents. The residue was distilled. Yield 50.3 g (44.5%).

B.p. 166-168° (2 mm), d^{20}_4 1.1400, $n^{20}D$ 1.4776, MR_D 78.43; calc. 76.44 (for the ketone form), 77.49 (for the enol form).

Found %: C 56.66, 56.53; H 7.49, 7.57. $C_{18}H_{24}O_7$. Calculated %: C 56.96; H 7.65.

Ethyl α-methyl-β-(β'-carbobutoxyethyl)-β-carbethoxylevulinate (II, R = C_4H_9). a) From the ethyl β-carbobutoxyethylacetoacetate (III, R = C_4H_9). The sodium derivative of ethyl β-carbobutoxyethylacetoacetate obtained from 4.45 g of sodium and 49.6 g of ethyl β-carbobutoxyacetoacetate in 250 ml of absolute ether was heated with 31 g of ethyl α-bromopropionate. The precipitate was dissolved in 70 ml of water. The ether layer was separated and the substance was extracted from the water with 100 ml of ether. After drying with sodiim sulfate and removal of the solvent, the residue was distilled. Yield 24.8 g (36.1%).

B.p. 174-176° (3 mm), d^{20}_4 1.081, $n^{20}D$ 1.4620, MR_D 91.18; calc. 90.29 (for the ketone form), 91.33 (for the enol form).

Found %: C 60.49; H 8.44. $C_{18}H_{30}O_7$. Calculated %: C 60.33; H 8.44.

b) From ethyl α-methyl-β-carbethoxylevulinate. To the sodium derivative of ethyl α-methyl-β-carbethoxylevulinate obtained from 1 g of sodium and 10 g of ethyl α-methyl-β-carbethoxylevulinate in 35 ml of absolute ether we added 7.35 g of butyl β-chloropropionate and heated on a water bath for 24 hr. After the usual treatment we obtained ethyl α-methyl-β-(β'-carbobutoxyethyl)-β-carbethoxylevulinate. Yield 0.8 g (5.13%). B.p. 174-176°, $n^{20}D$ 1.4620.

Found %: C 60.43; H 8.32. $C_{18}H_{30}O_7$. Calculated %: C 60.33; H 8.44.

Ethyl α-methyl-β-(β'-carboxyethyl)-levulinate (IV). We heated 9.2 g of ethyl α-methyl-β-(β'-carbomethoxyethyl)-β-levulinate with 11.2 g of hydrochloric acid (d 1.17) and 1.32 ml of water on a boiling water bath for four hours. The excess hydrochloric acid was distilled off. The residue was dissolved in 20 ml of water and extracted with 150 ml of ether. After drying with sodium sulfate the solvent was distilled off and the residue was fractionated. Yield 0.7 g (12%).

B.p. 119-120° (1 mm), d^{20}_4 1.1490, $n^{20}D$ 1.4710, MR_D 56.06; calc. 56.19 (for the ketone form), 57.24 (for the enol form).

Found %: C 57.27; H 8.10. $C_{11}H_{18}O_5$. Calculated %: C 57.36; H 7.87.

SUMMARY

1. We have carried out the synthesis of ethyl α-methyl-δ-(β'-carboxyethyl)-levulinate.

2. In the case of acetoacetic ester we have found the same relation of influence of order of addition for the alkyl substituents as with malonic ester, that is, the radical of β-chloropropionic acid should be introduced in the first step of the alkylation.

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SYNTHETIC STUDIES IN THE FIELD OF COENZYNE A

I. SYNTHESIS OF β-AMINOPROPIONIC ACID, β-ALANINE

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The β-aminopropionic radical is contained in the molecule of many natural biologically active substances, such as enzymes, pantetheine, coenzyme A, etc.

In connection with a study on the preparation of pantetheine and coenzyme A we have investigated the synthesis of β-alanine. Several methods of preparation are known for this compound: from succinimide, cyanoacetic ester [1-3], acrylonitrile by amidation with phthalimide in the presence of trimethylphenylammonium hydroxide [4], and trimethylbenzylammonium hydroxide, ethylene cyanohydrin [5], acetylene [6], tetrachloropropane [7], by hydrolysis of acrylamide polymer [8], and others. However, these methods lead to the synthesis of salts of β-aminopropionic acid. Obtaining free alanine from them is quite difficult.

For the synthesis of β-alanine we have used the phthalimide method, in which we have introduced a number of changes which permit getting a good yield of β-aminopropionic acid hydrochloride and free β-alanine.

The reaction of acrylonitrile with phthalimide in alcohol solution of sodium hydroxide gives phthalimidopropionitrile, which we hydrolyzed with dilute hydrochloric acid. The resulting β-aminopropionic acid hydrochloride was converted into free β-alanine by ion exchange on a monofunctional sulfocationite. The use of cationite KU-2 (exchange capacity established by us 0.297 g/ g) permitted isolation with a yield of 92% of free β-alanine from the technical product which was a mixture of β-alanine hydrochloride and ammonium chloride.

EXPERIMENTAL

1. Phthalimidopropionitrile (I). A solution of 200 g of phthalimide, 540 g of acrylonitrile, and 70 ml of 1% alcoholic solution of sodium hydroxide was heated to boiling for one hour. The crystals which precipitated on cooling were separated and washed with 100 ml of water, 75 ml of methyl alcohol, and were dried at 70-80°. We obtained 232 g of phthalimidopropionitrile. Excess acrylonitrile (365 g) was distilled from the filtrate. The crystals which precipitated on cooling were filtered, washed with 30 ml of water, 20 ml of methyl alcohol, and were dried. We further obtained 28.58 g of substance. The total yield was 260.58 g (95.7%). M.p. 153-154°.

Found %: C 66.07; H 4.24; N 13.90. $C_{11}H_8O_2N_2$. Calculated %: C 65.99; H 4.03; N 13.90.

2. β-Aminopropionic acid hydrochloride (II). Forty g of phthalimidopropionitrile in 340 ml of dilute (1 : 1) hydrochloric acid (d 1.098) was boiled for 3.5 hr. The precipitate of phthalic acid which separated on cooling was separated (31.6 g, 79.8%, m.p. 195-197°), washed with 50 ml of water, and dried at 100°. The colorless filtrate was evaporated in a vacuum (15 mm). The residue was recrystallized from isopropyl alcohol and dried at 70-80°. Yield 20.43 g (81.3%). M.p. 121.5-123°.

Found %: C 28.79; H 6.46; N 10.89; Cl 28.15. $C_3H_8O_2NCl$. Calculated %: C 28.69; H 6.42; N 11.16; Cl 28.23.

3. β-Aminopropionic acid, β-alanine. Through a column (diameter 3 cm, height 74 cm) filled with 150 g of ionite KU-2, a type of monofunctional sulfocationite, was passed a solution of 50 g of β-alanine hydrochloride in 450 ml of water at a rate of 1.5 ml/ min·cm^2. Then the ionite was washed with water (to a negative reaction for chloride ion), after which it was washed out with 2% ammonia solution (3 liters) at a rate of 2 ml/ min·cm^2. The eluate was concentrated to 1/3 the original volume and treated with activated charcoal. The colorless filtrate was evaporated. Yield 32.6 g (92.2%). M.p. 199-200° (from water).

Found %: C 41.00; H 7.66; N 15.65. $C_3H_7O_2N$. Calculated %: C 40.44; H 7.72; N 15.73.

SUMMARY

We have carried out the synthesis of β-aminopropionic acid, β-alanine, using the ion exchange resin KU-2.

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CONJUGATION FACTORS IN CYCLIC SYSTEMS

I. THE NATURE OF ISOMERIZATION OF DOUBLE BONDS IN MONOSUBSTITUTED CYCLOHEXADIENE-1,2-DICARBOXYLIC ACIDS

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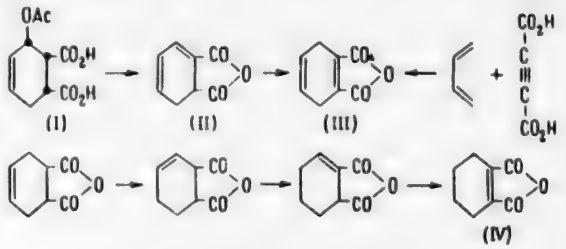
Original article submitted March 12, 1960

As has been shown previously [1], in the pyrolysis of cis-cis-3-acetoxy-Δ^4-cyclohexene-1,2-dicarboxylic acid (I) instead of the expected anhydride (II), there is obtained its isomeric anhydride (III) with an unconjugated $\Delta^{1,4}$-system of double bonds, identical with the adduct formed in the diene condensation of butadiene with acetylene dicarboxylic acid [2]. A similar isomerization of the anhydride from the $\Delta^{4,5}$-double bonds was found by Baeyer [3], who showed that the anhydrides of all possible isomeric cyclohexadiene-1,2-dicarboxylic acids were converted into anhydride (III) by heating to 180-200°.

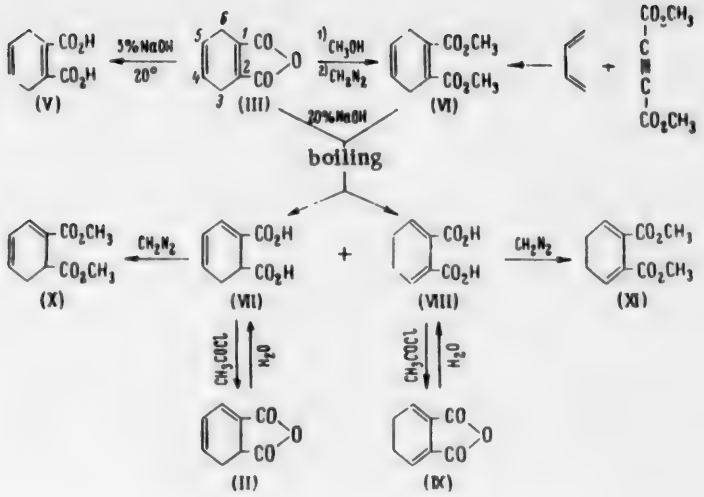


Similar regularities were studied in great detail in the case of isomers of cyclohexene-1,2-dicarboxylic acids where it was shown that heating their anhydrides with platinum on carbon [4] or with phosphoric anhydride [5] led to successive shifts of the double bond to the more stable Δ^1-position with the formation of system (IV).

In studying the chemical transformations of the anhydride of $\Delta^{1,4}$-cyclohexadiene-1,2-dicarboxylic acid (III) we established that the anhydride ring in it is quite stable and only by careful hydrolysis with a 5% alkali solution can the corresponding acid (V) be obtained. Boiling the anhydride (III) with methanol followed by treatment with diazomethane gives the corresponding diester (VI) which is identical with the product formed in the diene condensation of butadiene with dimethyl acetylene dicarboxylate. A characteristic peculiarity of the acid (V) and the diester (VI) is the instability of their system of $\Delta^{1,4}$-double bonds. Boiling these products with 20% sodium hydroxide causes isomerization of the double bond and leads to a mixture of known [2, 3] cyclohexadiene-1,2-dicarboxylic acids (VII) and (VIII) whose ratio under standard conditions of saponification (three hour boiling with 20% NaOH) is about 1 : 7.*

The isomeric acids (VII) and (VIII) under the action of acetyl chloride give the corresponding crystalline anhydrides (II) and (IX) and on treatment with diazomethane give the corresponding diesters (X) and (XI) whose saponification by alkali leads to a mixture again of the same two acids. This comparatively easy isomerization of the system of double bonds in the cyclohexadiene system has often been insufficiently considered in a number of previous works [7, 8].

*In this and the analogous cases described below we are evidently dealing with a reversible isomerization of acids (VII) and (VIII) of the type of equilibrium in a pentad system [6]. However, in the present communication we describe only the results of isomerization under standard conditions (three hour boiling with 20% NaOH solution) which permits us to judge only the direction of isomerization. The composition of the equilibrium mixture and kinetics of the isomerization process are being studied.



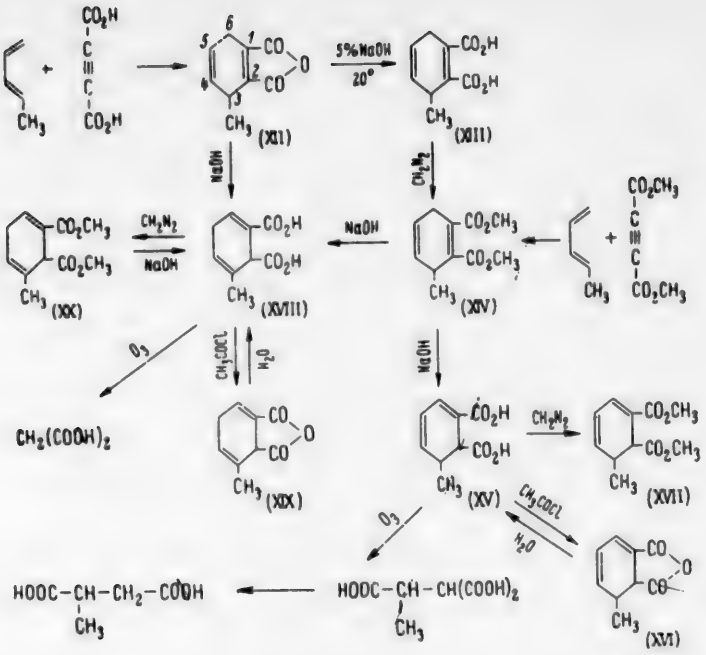
All the transformations described above show that in $\Delta^{1,4}$-cyclohexadiene-1,2-dicarboxylic acid (V) the double bonds lying between the carbonyl groups are stable only in the presence of the anhydride ring and when it is opened they can isomerize into the Δ^{6}-position with formation of the conjugated system of $\Delta^{4,6}$-double bonds. Since this shift of the double bond into the Δ^{6}-position is also characteristic for Δ^{1}-cyclohexene-1,2-dicarboxylic acid [9] we can consider that the chief reason for such isomerization is obviously not only the tendency to conjugation with the double bond on C_4 but also the spacial hindrances which occur in opening the planar anhydride ring.

Consideration of the molecular model shows that in transformation from $\Delta^{1,4}$-anhydride (III) to $\Delta^{1,4}$-diester (VI) the system of C = O bonds of the carbomethoxy group and the C = C bond between them cannot be coplanar, which destroys one of the basic conditions for realization of the π-conjugation. In correspondence with this the system (VII) becomes energetically more favorable, occurring as the result of a shift of the double bond in the Δ^{6}-position in which there can be realized normally a conjugation of the C = C bonds among themselves and with the C = O bond of one of the carboxymethyl groups. For this reason system (VIII) becomes more favorable, the formation of which occurs with more severe conditions of saponification.

In order to explain the effect of substituents on the character of the shift of the double bond in cyclohexadiene-1,2-dicarboxylic acid we synthesized its homologs containing methyl groups in different positions in the ring. As the first object of investigation we chose the anhydride of 3-methyl-$\Delta^{1,4}$-cyclohexadiene-1,2-dicarboxylic acid (XII), obtained in the diene condensation of transpiperylene with acetylene dicarboxylic acid. This anhydride was quite stable and was only saponified by long boiling with aqueous acetone to give the corresponding acid (XIII); this by treatment with diazomethane gave the diester (XIV) which in turn could be obtained by diene condensation of piperylene with diethyl acetylene dicarboxylate.

We showed that when the diester (XIV) was saponified by boiling with 20% sodium hydroxide, the chief reaction product was 3-methyl-$\Delta^{4,6}$-cyclohexadiene-1,2-dicarboxylic acid (XV), characterized by the anhydride and the diester (XVII). The structure of acid (XV) was shown by ozonization [10] into the known propane-1,1,2-tricarboxylic acid which on decarboxylation gave methyl succinic acid. The presence of the conjugated system of double bonds in acid (XV) was also confirmed by the ultraviolet spectrum (λ_{max} 288 mμ; log ε 3.671). All these results show that acid (XV) and its derivatives have a $\Delta^{4,6}$-arrangement of double bonds and alkaline saponification of diester (XIV) is accompanied by a shift of the Δ^{1}-double bond into the unsubstituted Δ^{6}-position.

In one of the previous studies [11] the product obtained in the alkaline saponification of diester (XIV), without special evidence, was assigned the structure of 3-methyl-$\Delta^{1,4}$-cyclohexadiene-1,2-dicarboxylic acid.



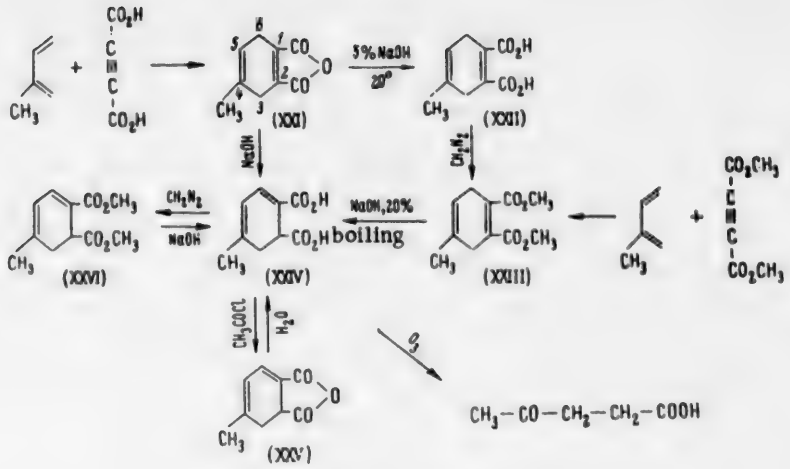
Alkaline saponification of anhydride (XII) also occurred with a shift of double bonds. However, in this case, isomerization was accompanied by a more complex rearrangement, and the chief reaction product (over 50%) was a new dicarboxylic acid (XVIII) which also was formed in small amount in saponification of the diester (XIV). This acid gave its anhydride (XIX) and diester (XX), had no absorption in the region 220-310 mμ, and on ozonization gave malonic acid. It could easily add two moles of hydrogen in the presence of a Pd catalyst, which confirmed the absence in it of a double bond in the Δ^1- and Δ^2-positions. All these results show that acid (XVIII) has as the sole possibility for its structure 3-methyl-$\Delta^{3,6}$-cyclohexadiene-1,2-dicarboxylic acid and its formation occurs as a result of a simultaneous shift of the $\Delta^{1,4}$-double bonds to the carbon atoms C_6 and C_3.

The system of double bonds in acid (XVIII) is quite stable to alkali: after three hour boiling of the diester (XX) with 20% sodium hydroxide there is practically no formation of an acid of type (VIII) with $\Delta^{2,6}$-arrangement of the double bonds, and acid (XVIII) is recovered in 55% yield. More than this, alkaline saponification of the isomeric diester (XVII) with a conjugated system of double bonds of the ring is accompanied by isomerization and leads to 3-methyl $\Delta^{3,6}$-cyclohexadiene-1,2-dicarboxylic acid (XVIII) with yields of about 25%.

These facts show that in the presence of a methyl group on C_3 the stable product of isomerization of cyclohexene-1,2-dicarboxylic acids can be the system (XVIII) with a nonconjugated arrangement of double bonds. An analogous isomerization was found previously in the case of dihydroterephthalic acid [12].

In connection with an effect of specific "inhibition" of the shift of the double bonds in the presence of a methyl group on C_3 we have studied the alkaline isomerization of 4-methyl-$\Delta^{1,4}$-cyclohexadiene-1,2-dicarboxylic acid (XXII) obtained by careful alkaline hydrolysis of the anhydride (XXI) which is easily formed as the result of diene condensation of isoprene with acetylene dicarboxylic acid (see scheme below).

We showed that the corresponding diester (XXIII), also obtained by condensation of isoprene with dimethyl acetylene dicarboxylate, when boiled with 20% sodium hydroxide gives a yield of 65% of only one isomer, 4-methyl-$\Delta^{4,6}$-cyclohexadiene-1,2-dicarboxylic acid (XXIV), characterized as its anhydride (XXV) and diester (XXVI). Previously this acid was erroneously ascribed the structure of the normal product of the diene synthesis [11, 13]. The structure of the acid (XXIV) was shown by ozonization, as a result of which we isolated levulinic acid, and was confirmed by the ultraviolet spectrum (λ_{max} 296 mμ, log ε 3.903). Alkaline hydrolysis of the anhydride (XXI) also gave only the acid (XXIV), and products of deeper rearrangement of the double bonds could not be isolated in this case. Evidently their formation was hindered by the presence of the methyl group on the Δ^4-double bond.



EXPERIMENTAL

I. $\Delta^{1,4}$-Cyclohexadiene-1,2-dicarboxylic Acid (V), Its Anhydride (III) and Diester (VI) and Their Reactions

1. Anhydride of $\Delta^{1,4}$-cyclohexadiene dicarboxylic acid (III). A mixture of 15 g of acetylene dicarboxylic acid, 25 ml of divinyl, 48 ml of dioxane, and 0.2 g of pyrogallol was heated 5.5 hr in a steel cylinder at 100°. The dioxane was distilled from the reaction mixture in a vacuum and the crystalline residue was washed on the filter with a small amount of ether. We obtained 10.8 g (54%) of anhydride (III) with m.p. 145-146° (from ethyl acetate), which agreed with the literature data [2]. Anhydride (III) was recovered unchanged after 15 min boiling in water, and was also not changed on two hour heating in a stream of nitrogen at 200°.

Saponification of anhydride (III) with 5% NaOH at room temperature led to known $\Delta^{1,4}$-cyclohexadiene-1,2-dicarboxylic acid (V) with m.p. 152-153° [2].

When acid (V) was treated with an ether solution of diazomethane by the usual method, we obtained its dimethyl ester (VI).

B.p. 137-138° (10 mm), $n^{20}D$ 1.4942, d^{20}_4 1.1733.

Found %: C 61.32, 61.53; H 6.21, 6.40. $C_{10}H_{12}O_4$. Calculated %: C 61.21; H 6.16.

The same diester (VI) was obtained with a yield of 84% by diene condensation of dimethyl acetylene dicarboxylate with 1,3-butadiene.

2. Alkaline saponification of the diester (VI). A mixture of 6.1 g of diester (VI) with 30 ml of 20% KOH was boiled for three hours. The solution was cooled, filtered, and acidified with hydrochloric acid; it was left standing for 15 hr. The resulting crystalline precipitate was filtered off, washed with water, and dried in air. We obtained 2.52 g of a mixture of acids with m.p. 185-186° (A). The mother liquor was extracted with ether, the ether extract was dried with Na_2SO_4, and was evaporated to dryness in a vacuum. The residue was washed with a small amount of water, and we obtained 2.4 g of a mixture of acids with m.p. 145-160° (B).

For the extraction of individual acids from the mixture of products "A" it was mixed with 25 ml of acetic chloride and allowed to stand for a day at room temperature. The insoluble substance was filtered off, washed with acetyl chloride, and dried in a vacuum; we obtained 0.35 (6.7%) of $\Delta^{2,6}$-cyclohexadiene-1,2-dicarboxylic acid (VIII) with m.p. 213° (decomp.) (from water) which agrees with the literature data [2]. The mother liquor was evaporated dry in a vacuum, the crystalline residue was washed on the filter with a mixture of ether and ligroin (1 : 1) and we obtained 1.5 g of anhydride of $\Delta^{2,4}$-cyclohexadiene-1,2-dicarboxylic acid (II) with a constant m.p. 100-101° which agreed with the literature [2].

On saponification of the anhydride (II) by boiling with water we obtained an acid (VII) with m.p. 179-180° (decomp) which also agreed with the literature data [2]. A further amount of anhydride (II) was isolated from mixture "B" as follows: product "B" was recrystallized from water and we obtained a mixture of acids with m.p. 163-166°

(1.1 g) which was treated as described above with acetyl chloride. The resulting solution was evaporated dry in a vacuum and the crystalline residue was washed with a mixture of ether and ligroin (1 : 1). We obtained 0.65 g of anhydride (II) with m.p. 97-98°, which gave no depression of the melting point with the form described above.

Acid (VII) gave the diester (X) when treated in ether solution with diazomethane.

B.p. 128-129° (8.5 mm), $n^{20.2}D$ 1.5064, d^{20}_4 1.174, MR_D 48.56; calc. 49.64.

Found %: C 61.06, 60.91; H 6.22, 6.15. $C_{10}H_{12}O_4$. Calculated %: C 61.22; H 6.16.

3. Alkaline saponification of anhydride (III). A mixture of 0.85 g of anhydride (III) with 4 g of 20% NaOH solution was boiled for three hours. The solution was filtered and acidified with hydrochloric acid to an acid reaction to Congo. The crystals which precipitated were filtered off and washed with water. We obtained 0.63 g of a mixture of crystalline acids with m.p. 177-183°. The mixture was treated with acetyl chloride as described above in the experiment on alkaline saponification of diester (VI), and we obtained 0.35 g (36%) of $\Delta^{2,6}$-cyclohexadiene-1,2-dicarboxylic acid (VIII) with m.p. 207-210° (decomp.) (from water), which gave no melting point depression with the form described above. We isolated from the mother liquor 0.15 g of the anhydride of $\Delta^{4,6}$-cyclohexadiene-1,2-dicarboxylic acid (II), identical with the form described above.

II. 3-Methyl-$\Delta^{1,4}$-cyclohexadiene-1,2-dicarboxylic Acid (XIII), Its Anhydride (XII) and Diester (XIV) and Their Reactions

1. Anhydride of 3-methyl-$\Delta^{1,4}$-cyclohexadiene-1,2-dicarboxylic acid (XII). A mixture of 7 g of acetylene dicarboxylic acid, 15 ml of piperylene, 50 ml of dioxane, and 0.2 g of picric acid was heated for 23 hr at 50-55°. The solvent and excess diene were distilled off in a vacuum and the residue crystallized on standing. The crystals were filtered off, washed with a mixture of ether and ligroin (1 : 2), and we obtained 6.75 g of a mixture of 3-methyl-$\Delta^{1,4}$-cyclohexadienedicarboxylic acid (XIII) with its anhydride (XII) with m.p. 56-80°, from which by vacuum distillation we obtained 5.5 g of anhydride (XII) with m.p. 56-58°. Evaporation of the wash ether solution gave a further 0.75 g of anhydride (XII) with m.p. 56-58°. After recrystallization from a mixture of ether and ligroin (1 : 4) the anhydride had m.p. 61-62°. Total yield of product 6.25 g (60%).

Found %: C 66.02; H 4.78. $C_9H_8O_2$. Calculated %: C 65.85; H 4.91.

2. 3-Methyl-$\Delta^{1,4}$-cyclohexadiene-1,2-dicarboxylic acid (XIII). a) A mixture of 1.23 g of anhydride (XII) and 2 ml of 10% aqueous acetone was boiled for five hours. The acetone was distilled off and when the reaction mixture was cooled, acid (XIII) crystallized out, m.p. 113-114.5° (from water).

Found %: C 59.05, 59.06; H 5.45, 5.48. M 181.6 by titration with NaOH. $C_9H_{10}O_4$. Calculated %: C 59.33; H 5.53. M 182.

b) We shook 0.5 g of anhydride (XII) for 2.5 hr with 10 ml of a 10% soda solution. The solution was evaporated in a vacuum to a volume of 5 ml, acidified, and allowed to stand for 15 hr. The crystals which precipitated were filtered off and washed with water. We obtained 0.45 g of acid (XIII) with m.p. 109-111°, giving no melting point depression with the form described above. When acid (XIII) was boiled for 0.5 hr with acetyl chloride it quantitatively formed the starting anhydride (XII) with m.p. 57-59°.

3. Dimethyl ester of 3-methyl-$\Delta^{1,4}$-cyclohexadiene-1,2-dicarboxylic acid (XIV). a) To a solution of 10 g of dimethyl acetylene dicarboxylate in 40 ml of dioxane was added 0.2 g of picric acid and 20 ml of piperylene. The reaction mixture was heated for five hours in a steel cylinder at 100-110°, after which the solvent was distilled off and the residue was distilled in a vacuum. We obtained 11.3 g (71%) of reaction product with b.p. 95.5-99° (3 mm), $n^{17}D$ 1.4904. After repeated distillations we isolated 10.5 g of diester (XIV).

B.p. 98-99.5° (3 mm), $n^{20}D$ 1.4891, d^{20}_4 1.1369, MR_D 53.35; calc. 52.93.

Found %: C 62.88, 62.72; H 6.80, 6.83. $C_{11}H_{14}O_4$. Calculated %: C 62.84; H 6.71.

b) Four g of anhydride (XII) was boiled for two hours with 20 ml of methanol. The solution was evaporated to a volume of 5 ml and treated with an ether solution of diazomethane. The solvent was distilled off and the residue was distilled in a vacuum. We obtained 4 g of diester (XIV) with $n^{17}D$ 1.4901.

4. Alkaline saponification of diester (XIV); 3-methyl-$\Delta^{4,6}$-cyclohexadiene-1,2-dicarboxylic acid (XV) and its derivatives. A mixture of 6 g of diester (XIV) and 30 g of 20% NaOH solution was boiled for three hours. The

solution was filtered and acidified to Congo with hydrochloric acid. The crystals which precipitated were filtered off, washed with water, and dried in air. We obtained 3.62 g of a mixture of acids with m.p. 162-166°. For purification the product was mixed with 20 ml of acetyl chloride and allowed to stand for 40 hr. The solution was filtered and the acetyl chloride was distilled off in a vacuum. The crystalline residue was washed on the filter with a small amount of ether. We obtained 1.88 g of anhydride of 3-methyl-$\Delta^{4,6}$-cyclohexadiene-1,2-dicarboxylic acid (XVI) with m.p. 99-103°. On evaporation of the wash ether we isolated a further 0.7 g of anhydride (XVI) with m.p. 95-97°, which gave no melting point depression with the form described above. After recrystallization from a mixture of ether and ligroin (1 : 1) anhydride (XVI) melted at 107-108°.

Found %: C 65.86, 65.70; H 4.90, 4.93. $C_9H_8O_3$. Calculated %: C 65.85; H 4.91.

On boiling a mixture of 6 g of diester (XIV) and 60 g of 20% NaOH solution we were able to isolate by treatment analogous to that above both anhydride (XVI) and the dicarboxylic acid (XVIII) which is more difficultly soluble in acetyl chloride and melts at 217-219° (decomp.) (see below).

To obtain acid (XV), 0.3 g of anhydride (XVI) was boiled for 15 min with 2 ml of 20% aqueous acetone. The acetone was distilled off, the solution was cooled in ice water, and the crystals which precipitated were filtered off. We obtained 0.18 g of 3-methylcyclohexadiene-1,2-dicarboxylic acid (XV) with m.p. 189-190.5° (from acetonitrile).

Found %: C 59.15, 59.14; H 5.54, 5.47. $C_9H_{10}O_4$. Calculated %: C 59.33; H 5.53.

On boiling acid (XV) with acetyl chloride for three hours the starting anhydride (XVI) was formed with a quantitative yield. Boiling a mixture of acid (XV) with acetic anhydride gave quantitative formation of anhydride (XII) with m.p. 59-60°, giving no melting point depression with the form described above.

5. Ozonization of acid (XV). A stream of oxygen enriched with ozone (amount of ozone 0.5 g/ hr) was passed for 7.5 hr at 0° through a solution of 1.4 g of acid (XV) in 60 ml of 96% aqueous acetic acid. Ten ml of 70% peracetic acid was added to the reaction mixture and the solution was kept for 18 hr at 45-50°. The low boiling products were distilled in a vacuum and the residue gradually crystallized on successive distillations with benzene. The crystals were filtered off and washed with a mixture of ether and benzene (1 : 1). We obtained 0.6 g of ozonization product with m.p. 127-131° (decomposition). After recrystallization from a mixture of ether and ligroin (1 : 1) we obtained 0.3 g of 1,1,2-propane tricarboxylic acid with m.p. 150-151° (decomposition) (according to the literature, m.p. 146° [14]).

We isolated a further 0.2 g of the same acid from the mother liquors. The total yield was 0.5 g (37%).

Found M 175.0 (by titrating with NaOH). $C_6H_8O_4$. Calculated M 178.

We heated 0.25 g of 1,1,2-propane tricarboxylic acid at 165-170° to full cessation of evolution of CO_2 (30 min). The melt solidified at once when cooled. The crystalline product was washed with benzene and gave 90 mg (50%) of methyl succinic acid with m.p. 111-112°, giving no melting point depression with a known sample.

6. Dimethyl ester of 3-methyl- $\Delta^{4,6}$-cyclohexadiene-1,2-dicarboxylic acid (XVII) and its alkaline saponification. In order to obtain the diester (XVII) 2.1 g of anhydride (XVI) was boiled for three hours with 30 ml of methanol. The solution was evaporated in a vacuum to a volume of 5 ml and treated with an ether solution of diazomethane. The solvent was distilled off and the residue was distilled in a vacuum. We obtained 2.2 g of the diester (XVII) with b.p. 130-131° (8 mm), $n^{17.5}_D$ 1.5040.

Found %: C 62.97, 62.71; H 6.72, 6.58. $C_{11}H_{14}O_4$. Calculated %: C 62.84; H 6.71.

A mixture of 1.35 g of diester (XVII) was boiled for 6 hr with 13.5 g of 20% NaOH solution. The solution was filtered, acidified with hydrochloric acid, and allowed to stand for 15 hr. The crystals which precipitated were filtered off, washed with water, and dried in air. We obtained 0.6 g of a mixture of acids with m.p. 165-175°. After two recrystallizations from 20% aqueous acetone we obtained 0.27 g (24%) of 3-methyl-$\Delta^{3,6}$-cyclohexadiene-1,2-dicarboxylic acid (XVIII) with m.p. 214-216°, giving no melting point depression with the form described below (see part 7).

7. Alkaline saponification of anhydride (XII); 3-methyl-$\Delta^{3,6}$-cyclohexadiene-1,2-dicarboxylic acid (XVIII), its anhydride (XIX) and diester (XX). A mixture of 5.16 g of anhydride (XII) with 50 g of 20% NaOH solution was boiled for three hours. The resulting solution was cooled, filtered, acidified to Congo with hydrochloric acid, and allowed to stand for 15 hr. The crystals which precipitated were filtered off and washed with water. We obtained

3.65 g of a mixture of acids with m.p. 186-190°. After crystallization from 12% aqueous acetone we obtained 2.65 g (46%) of 3-methyl-$\Delta^{3,6}$-cyclohexadiene-1,2-dicarboxylic acid (XVIII) with m.p. 212-213° (decomp.). Repeated recrystallizations gave a product with m.p. 217-219° (decomp.).

Found %: C 59.44, 59.28; H 5.55, 5.48. M 180 (by titration with NaOH). $C_9H_{10}O_4$. Calculated %: C 59.33, H 5.53, M 182.

To obtain the corresponding anhydride we boiled 0.2 g of acid (XVIII) for 30 min with 15 ml of acetyl chloride. The solution was evaporated dry in a vacuum, the residue was washed on the filter with a mixture of ether and ligroin (1 : 2); we obtained 0.15 g of the anhydride of 3-methyl-$\Delta^{3,6}$-cyclohexadiene-1,2-dicarboxylic acid (XIX) with m.p. 85-86° (from a 1 : 1 mixture of ether and ligroin).

Found %: C 66.18, 66.11; H 4.59, 4.67. $C_9H_8O_3$. Calculated %: C 65.84; H 4.91.

On saponification of anhydride (XIX) with 20% aqueous acetone acid (XVIII) was formed quantitatively with m.p. 208-210°, giving no melting point depression with the form described above.

In order to obtain the diester (XX) we dissolved 2.65 g of the dicarboxylic acid (XVIII) in 5 ml of methanol and treated it with an ether solution of diazomethane. The solvent was distilled off and the residue was distilled in a vacuum. We obtained 2.5 g of the diester (XX) with b.p. 121-123° (5 mm), $n^{18}D$ 1.4930.

Found %: C 62.70, 62.60; H 6.56, 6.63. $C_{11}H_{14}O_4$. Calculated %: C 62.84; H 6.71.

When a mixture of 0.8 g of this diester was boiled for three hours with 7 g of 20% sodium hydroxide solution we obtained 0.35 g of the corresponding $\Delta^{3,6}$-acid (XVIII) with m.p. 204-205° (decomp.), not giving a melting point depression with the form described above.

8. Hydrogenation of acid (XVIII). We hydrogenated 0.22 g of acid (XVIII) in methanol over Pd/$CaCO_3$. The amount of hydrogen calculated for two double bonds was absorbed. The solution was filtered, evaporated dry in a vacuum and the crystalline residue was washed on the filter. We obtained 0.18 g of cis-cis-3-methylcyclohexane-1,2-dicarboxylic acid with a m.p. 161-162° (from water), giving no melting point depression with a known sample.

9. Ozonization of acid (XVIII). A stream of ozonized oxygen (amount of ozone 0.5 g/hr) was passed for 5.5 hr at 0° into a solution of 1.5 g of acid (XVIII) in 55 ml of 95% aqueous acetic acid. The reaction mixture was treated with 10 ml of 70% peracetic acid and the solution was heated for 20 hr at 45-50°. Acetic and paracetic acids were distilled off in a vacuum and the residue, at first liquid, gradually crystallized. The crystalline product was filtered, washed with a mixture of benzene and ether and gave 0.35 g of substance with m.p. 110-112° (decomp.). After recrystallization from a mixture of benzene and ether (1 : 1) we isolated 0.15 g of a substance with m.p. 125° (decomp.) from which after repeated recrystallizations we obtained malonic acid with m.p. 132-133° (decomp.), not giving a melting point depression with a known sample.

III. 4-Methyl-$\Delta^{1,4}$-cyclohexadiene-1,2-dicarboxylic Acid (XXII), Its Anhydride (XXI) and Diester (XXIII)

1. Obtaining anhydride (XXI), acid (XXII) and diester (XXIII). a) A mixture of 5 g of acetylene dicarboxylic acid, 13 ml of isoprene, 25 ml of dioxane, and 0.2 g of pyrogallol was heated for 24 hr at 65-70°. The solvent and excess isoprene were distilled off in a vacuum and we obtained 4.9 g (68%) of anhydride (XXI) with m.p. 101-102° (from a small amount of ether).

Found %: C 65.54, 65.76; H 4.80, 4.84. $C_9H_8O_3$. Calculated %: C 65.85; H 4.91.

b) To obtain the acid (XXII) we suspended 1 g of anhydride (XXI) in 5 ml of water and boiled for three hours. The solution was cooled, whereupon the crystals of 4-methyl-$\Delta^{1,4}$-cyclohexadiene-1,2-dicarboxylic acid which precipitated were filtered off and washed with water. We obtained 0.9 g of acid (XXII) with m.p. 140-141° which did not change after repeated crystallizations from water.

Found %: C 59.11, 59.26; H 5.46, 5.46. $C_9H_{10}O_4$. Calculated %: C 59.33; H 5.54.

c) To a solution of 20 g of dimethyl acetylene dicarboxylate in 50 ml of anhydrous benzene we added 28 ml of isoprene and 0.2 g of pyrogallol; the reaction mixture was heated for four hours in a steel cylinder at 130-140°. The benzene was distilled off and the liquid residue was distilled in a vacuum. We obtained 27.1 g (90%) of the dimethyl ester of 4-methyl-$\Delta^{1,4}$-cyclohexadiene-1,2-dicarboxylic acid (XXIII) with b.p. 122.5-124° (3 mm),

$n^{18}D$ 1.4950, which corresponded to the values in the literature [10]. The same diester (XXIII) was obtained with a quantitative yield by treating a solution of acid (XXII) in methanol with an ether solution of diazomethane.

2. Alkaline saponification of the diester (XXIII). To 33 g of 20% NaOH solution was added 6.3 g of the diester and the mixture was boiled for 3.5 hr. The resulting solution was cooled, filtered, and acidified with hydrochloric acid. The crystals which precipitated were filtered off, washed with water, and dried. We obtained 3.56 g (65%) of 4-methyl-$\Delta^{4,6}$-cyclohexadiene-1,2-dicarboxylic acid (XXIV) with m.p. 205-207° (from 35% aqueous acetone, decomposition, slow heating from 200°).

Found %: C 59.29, 59.17; H 5.48, 5.48. $C_9H_{10}O_4$. Calculated %: C 59.36; H 5.54.

To obtain anhydride (XXV) we boiled 0.5 g of acid (XXIV) for two hours with 20 ml of acetyl chloride. The solution was evaporated dry in a vacuum, the residue was washed on the filter with a mixture of ether and ligroin (1 : 3) and we obtained 0.27 g of anhydride (XXV) with m.p. 95-96° (from ether).

Found %: C 65.72, 65.77; H 4.92, 5.00. $C_9H_8O_3$. Calculated %: C 65.85; H 4.91.

Saponification of anhydride (XXV) with water regenerated the starting acid (XXIV) with m.p. 205-207 (decomp.), not giving a melting point depression with the form described above.

When acid (XXIV) was treated with diazomethane it gave a quantitative yield of its dimethyl ester (XXVI) with b.p. 120-121°, $n^{20}D$ 1.5080.

Found %: C 62.48, 62.62; H 6.69, 6.55. $C_{11}H_{14}O_4$. Calculated %: C 62.85; H 6.71.

Ozonization of acid (XXIV). A stream of ozonized oxygen (amount of ozone 0.5 g O_3/ hr) was passed through a solution of 1.4 g of acid (XXIV) in 80 ml of 90% aqueous acetic acid at 0° for seven hours. We added to the reaction mixture 10 ml of 70% peracetic acid and kept for 22 hr at 45-50°. Acetic and peracetic acids were distilled off in a vacuum, the liquid residue was heated at 160-170° to complete cessation of CO_2 evolution, and was then distilled in a vacuum. We obtained 0.2 g (20%) of levulinic acid, characterized by the semicarbazone with m.p. 180° (decomp.) which gave no melting point depression when mixed with a known sample.

SUMMARY

1. We have studied the nature of the isomerization of the double bonds in alkaline saponification of the anhydrides and diesters of 3- and 4-methyl-$\Delta^{1,4}$-cyclohexadiene-1,2-dicarboxylic acids.

2. We have shown that the general rule for alkaline isomerization of all the systems studied is the shift of the Δ^1-double bond to the Δ^6-position, conjugated with the Δ^4-double bond; when substituents are present on C_3 this shift occurs only in the unsubstituted Δ^6-position.

3. We have shown that an unsubstituted Δ^4-double bond is also capable of isomerization; when a substituent is present on C_3 such isomerization leads to a system with nonconjugated double bonds.

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CONJUGATION FACTORS IN CYCLIC SYSTEMS

II. ISOMERIZATION OF DOUBLE BONDS IN DIMETHYL-$\Delta^{1,4}$-CYCLOHEXADIENE-1,2-DICARBOXYLIC ACIDS

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As we showed in the previous communication [1], the chief regularity in the alkaline isomerization of methyl-$\Delta^{1,4}$-cyclohexadiene-1,2-dicarboxylic acids was the tendency to shift the double bond on C_1 from a conjugated position with the two carboxyl groups into conjugation with the second double bond of the ring and such a shift occurred only in an unsubstituted position. In special cases there could be a shift of the double bond on C_4 also; however, such a shift took place only when here the double bond did not contain a substituent.

All these rules could easily be confirmed in the case of dimethyl substituted cyclohexadiene-1,2-dicarboxylic acids, and as the first object of investigation we chose 3,4-dimethyl-$\Delta^{1,4}$-cyclohexadiene-1,2-dicarboxylic acid (II). Its anhydride (I), easily obtained in the condensation of trans-3-methyl-2,4-pentadiene with acetylene dicarboxylic acid, was thermally stable and could not be saponified even on prolonged boiling with water. However, on treatment with 5% sodium hydroxide solution in the cold this anhydride gave the corresponding acid (II) whose ester (III) was obtained in good yield also in the condensation of 3-methyl-2,4-pentadiene with dimethyl acetylene dicarboxylate.

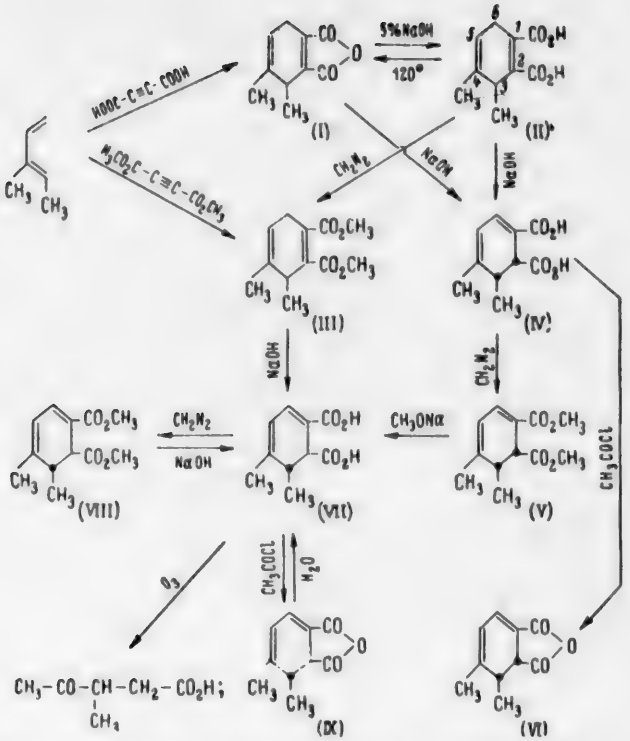
As a result of the study of the transformations of these derivatives it was established that when the anhydride (I) or the acid (II) was boiled with a 15% sodium hydroxide solution they easily formed the isomeric acid (IV) with a system of conjugated double bonds (λ_{max} 298 mμ, log ε 3.793), which gave the corresponding diester (V) and the crystalline anhydride (VI). However, on alkaline saponification of the diester (III), as one of the reaction products we obtained a new acid (VII), diester (VIII), and anhydride (IX), which differed from all those described above. This acid (VII) had the same absorption maximum in the ultraviolet (λ_{max} 297.5 mμ, log ε 3.904)* as did acid (IV) and thus has the same arrangement of conjugated double bonds (see scheme below).

When acid (VII) was ozonized we obtained in good yield only β-methyl levulinic acid which plainly shows the structure of (VII) as 3,4-dimethyl-$\Delta^{4,6}$-cyclohexadiene-1,2-dicarboxylic acid. Since its isomeric acid (IV) has the same arrangement of double bonds we can assume that acids (IV) and (VII) are geometrical isomers with the occurrence of centers of asymmetry at C_2 and C_3. In accord with this, one of these should be converted into the other by isomerization of its diester with sodium methylate, as was confirmed experimentally. It was shown that the diester (V) when isomerized by sodium methylate easily gave the acid (VII) which on this basis should have the trans-position of the carboxyl group on C_2 and the methyl group on C_3.

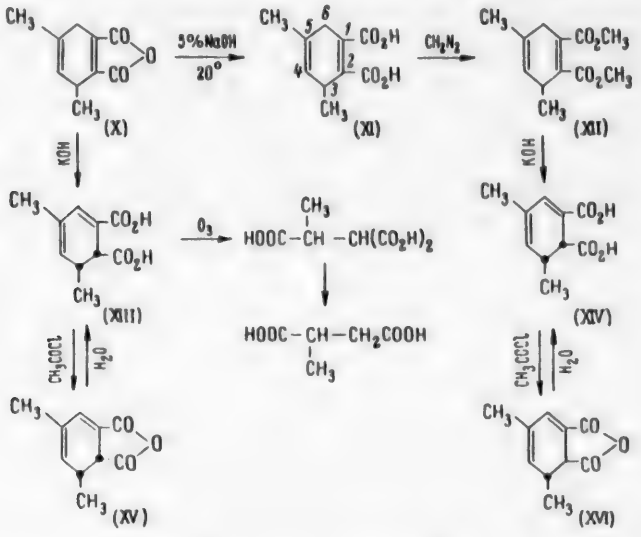
All these facts show that alkaline isomerization of 3,4-dimethyl-$\Delta^{1,4}$-cyclohexadiene-1,2-dicarboxylic acid (II) leads only to a shift of the double bond from the Δ^1-position into the unsubstituted Δ^6-position conjugated with another double bond. Thanks to the occurrence on this of two centers of asymmetry it becomes possible to form two geometric isomers; isomerization of the anhydride gives preference to the cis-isomer, and of the diester, to the trans-isomer.

An analogous rule for the isomerization of the double bonds and carboxyl groups exists in the case of 3,5-dimethyl-$\Delta^{1,4}$-cyclohexadiene-1,2-dicarboxylic acid (XI), anhydride (X), and diester (XII), which are easily obtained by condensation of 2-methyl-1,3-pentadiene with acetylene dicarboxylic acid and its diester. The anhydride (X), like the other anhydrides with the $\Delta^{1,4}$-position of the double bonds, is distinguished by the great stability of the

* The rules found in considering the ultraviolet absorption spectra of methyl- and dimethylcyclohexadiene-1,2-dicarboxylic acids and their functional derivatives will be discussed in a special communication.



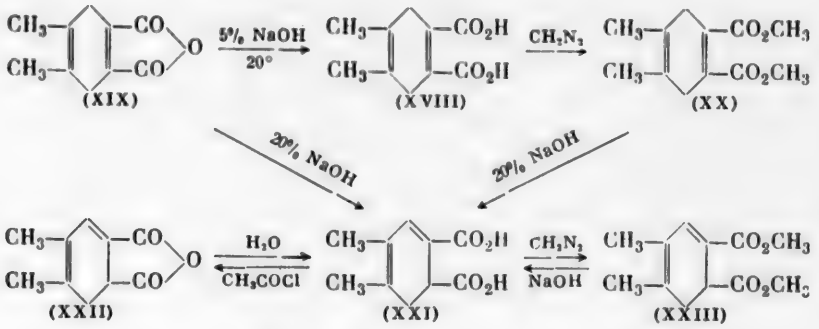
anhydride ring. It is saponified with formation of the corresponding acid (XI) only by treatment with a dilute NaOH solution in the cold. Moreover, acid (XI) can form the anhydride even by short boiling of its water solution.



We have shown that alkaline saponification of anhydride (X) and diester (XII) leads to the isomeric acids (XIII) and (XIV), which give the corresponding crystalline anhydrides (XV) and (XVI). These acids are characterized by the same position of the absorption maximum in the ultraviolet [λ_{max} 293 mμ, log ε 3.800 for (XIV); log ε 3.899 for (XIII)], which shows that they have the same arrangement of conjugated double bonds and thus can only be stereoisomers. On ozonization of acid (XIII) we obtained methyl succinic acid which shows the structure of both acids as geometrical isomers of 3,5-dimethyl-$\Delta^{4,6}$-cyclohexadiene-1,2-dicarboxylic acid. On the basis of the fact that the diester (XVII), which corresponds to acid (XIII), in alkaline hydrolysis forms as the chief reaction product acid (XIV), we can assign to this isomer the trans-configuration.

These results show that in the alkaline isomerization of 3,5-dimethyl-$\Delta^{1,4}$-cyclohexadiene-1,2-dicarboxylic acid the shift of the Δ^1-double bond occurs only into the unsubstituted Δ^6-position, as a result of which it becomes possible to form cis- and trans-3,5-dimethyl-$\Delta^{4,6}$-cyclohexadiene-1,2-dicarboxylic acids. Isomerization of the Δ^4-double bond does not occur in this case. Comparison of the results of alkaline isomerization of 3-methyl [1] and 3,5-dimethyl-$\Delta^{1,4}$-cyclohexadiene-1,2-dicarboxylic acids shows that for stabilization of the system of ring double bonds the chief value evidently lies in the effect of hyperconjugation.

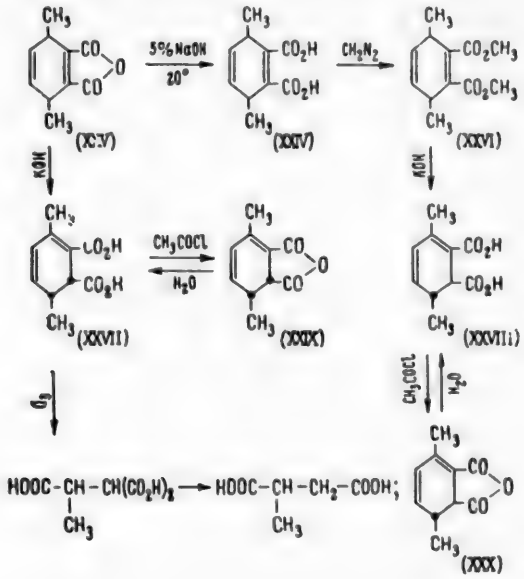
All the above regularities give sufficient basis for solving the problem of the structure of the products of alkaline isomerization of 4,5-dimethyl-$\Delta^{1,4}$-cyclohexadiene-1,2-dicarboxylic acid (XVIII).



(XIX) (XVIII) (XX) (XXII) (XXI) (XXIII)

In accord with the structure of this acid the shift in it of the Δ^1-double bond to the Δ^6-position should not lead to the occurrence of a new center of asymmetry, and so alkaline isomerization of its anhydride (XIX) and diester (XX) can give only one reaction product, which was confirmed experimentally. It was shown that when the anhydride (XIX) and the diester (XX) were boiled with 20% sodium hydroxide there was actually obtained the same acid (XXI), with a system of conjugated double bonds (λ_{max} 303 mμ, log ε 3.953) which formed the corresponding anhydride (XXII) and diester (XXIII). Alkaline hydrolysis of diester (XXIII) gave only acid (XXI) and no other isomerization product was found. All these results show that the acid (XXI) actually has the structure of a 4,5-dimethyl-$\Delta^{4,6}$-cyclohexadiene-1,2-dicarboxylic acid, since any other more complex shift of the double bond in the starting acid (XVIII) would inevitably lead to a mixture of geometrical isomers. We could not show the structure of this product by ozonization, since as a result of ozonolysis in this case high molecular weight products are formed which were not further studied. This fact agrees with the literature report on the anomalous ozonolysis of 1,2-dimethylcyclohexene [2].

It is of interest to study the direction of shift of the double bond in those disubstituted $\Delta^{1,4}$-cyclohexadiene-1,2-dicarboxylic acids which contain substituents in the allyl position to both double bonds.



(XXV) (XXVI) (XXVII) (XXIX) (XXVIII) (XXX)

For this purpose we chose 3,6-dimethyl-$\Delta^{1,4}$-cyclohexadiene-1,2-dicarboxylic acid (XXIV), anhydride (XXV), and diester (XXVI), which are easily obtained by the diene condensation of 1,4-dimethylbutadiene with acetylene dicarboxylic acid and its ester. We showed that in this system, in spite of the presence of substituents on C_3 and C_6, there could be a shift only of the Δ^1-double bond, and in alkaline saponification of the anhydride (XXV) and the diester (XXVI) there were formed the geometrical isomers of 3,6-dimethyl-$\Delta^{2,4}$-cyclohexadiene-1,2-dicarboxylic acid (XXVII) and (XXVIII), characterized by the corresponding anhydrides (XXIX) and (XXX). These acids have the same position for the absorption maximum in the ultraviolet [λ_{max} 285 mμ, log ε 3.793 for (XXVII) and log ε 3.846 for (XXVIII)], which also confirms the same position in them for the conjugated double bonds. Their structure was shown by ozonolysis which gave propane-1,1,2-tricarboxylic acid; this was decarboxylated to methyl succinic acid. By analogy with the above described regularities, acid (XXVIII), which is chiefly formed in the saponification of diester (XXVI), should have the trans-configuration.

Isomerization of 3,6-dimethyl-$\Delta^{1,4}$-cyclohexadiene-1,2-dicarboxylic acid (XXIV) goes much more slowly than does isomerization of acids not substituted in the β-position to the carboxyl group. In the products of alkaline saponification of acid (XXIV) under standard conditions there is still a considerable amount of the starting $\Delta^{1,4}$-acid and only with 8-10 hr boiling of the alkaline solution is isomerization complete.

Thus, the experimental results show that the characteristic peculiarity of chemical behavior of 3,6-dimethyl-$\Delta^{1,4}$-cyclohexadiene-1,2-dicarboxylic acid (XXIV) is the inability to isomerize of the unsubstituted Δ^4-double bond in it, and this difference from the previously described 3-methyl-$\Delta^{1,4}$-cyclohexadiene-1,2-dicarboxylic acid [1] requires further explanation.

EXPERIMENTAL

I. 3,4-Dimethyl-$\Delta^{1,4}$-cyclohexadiene-1,2-dicarboxylic Acid (II), Its Anhydride (I), and Diester (III)

1. Preparation of anhydride (I), acid (II), and diester (III). a) A mixture of 5 g of acetylene dicarboxylic acid, 6.5 ml of 3-methyl-2,4-pentadiene, 40 ml of absolute dioxane, and 0.2 g of pyrogallol was boiled for 5 hr. The dioxane was distilled off and the residue was distilled in a vacuum. We obtained 5.7 g (72%) of anhydride of 3,4-dimethyl-$\Delta^{1,4}$-cyclohexadiene-1,2-dicarboxylic acid (I) with b.p. 119-121° (4 mm), which crystallized on standing and had m.p. 46-47.5° (from ligroin).

Found %: C 67.30, 67.07; H 5.59, 5.64. $C_{10}H_{10}O_3$. Calculated %: C 67.37; H 5.67.

b) To obtain the acid (II) we added to the solution of 2.3 g of NaOH in 33 ml of water 4 g of anhydride (I) and shook the mixture to full solution. After distillation, the clear solution was evaporated in a vacuum to 3/4 its volume and the oil which separated gradually crystallized. The precipitate was filtered off, washed with a small amount of cold water, and dried. We obtained 3.7 g of 3,4-dimethyl-$\Delta^{1,4}$-cyclohexadiene-1,2-dicarboxylic acid (II) with, m.p. 100-101° (from a mixture of ether and ligroin 1 : 2).

Found %: C 60.92, 60.83; H 6.08, 6.12. $C_{10}H_{12}O_4$. Calculated %: C 61.20; H 6.17.

Acid (II) when heated for 30 min to 100-110° gives a quantitative yield of anhydride (I).

c) To obtain the diester (III) a mixture of 5 g of the diester of acetylene dicarboxylic acid, 5 g of 3-methyl-2,4-pentadiene, 30 ml of absolute dioxane and 0.2 g of pyrogallol was boiled for four hours. The dioxane was distilled off and the residue was distilled in a vacuum. We obtained 6 g (76%) of diester (III) with b.p. 135-136° (7 mm), $n^{20}D$ 1.4910.

Found %: C 64.20, 63.97; H 7.17, 7.14. $C_{12}H_{16}O_4$. Calculated %: C 64.27; H 7.19.

The same diester ($n^{20}D$ 1.4908) was obtained also by treating the acid (II) with an ether solution of diazomethane.

2. Alkaline saponification of anhydride (I). Cis-3,4-dimethyl-$\Delta^{4,6}$-cyclohexadiene-1,2-dicarboxylic acid (IV). To a solution of 3.4 g of NaOH in 23 ml of water we added 2.3 g of anhydride (I), boiled the mixture for one hour and allowed it to stand 15 hr. The solution was acidified with hydrochloric acid to an acid reaction to Congo, the crystalline product was filtered off, and gave 2.15 g of cis-3,4-dimethyl-$\Delta^{4,6}$-cyclohexadiene-1,2-dicarboxylic acid (IV) with m.p. 193-194° (from 40% aqueous acetone).

Found %: C 60.94, 60.85; H 6.06, 6.11. $C_{10}H_{12}O_4$. Calculated %: C 61.20; H 6.17.

The same acid (IV) was also obtained by boiling the anhydride (II) for three hours with a 15% NaOH solution.

To obtain the anhydride (VI) we boiled 0.15 g of acid (IV) for two hours with 10 ml of acetyl chloride. The solution was evaporated in a vacuum and the crystalline precipitate was washed with ligroin. We obtained 90 mg of anhydride (VI) with m.p. 65-67°, which after crystallization had m.p. 71-73° (from ligroin). Anhydride (VI) was unstable; when dried in a vavuum at 56° it decomposed.

When acid (IV) in methanol solution was treated with an ether solution of diazomethane it gave a quantitative yield of the corresponding diester (V) with b.p. 134-135° (4 mm), $n^{19}D$ 1.5070.

Found %: C 64.58, 64.53; H 7.33, 7.35. $C_{12}H_{16}O_4$. Calculated %: C 64.27; H 7.19.

3. Alkaline saponification of diester (III). Trans-3,4-dimethyl-$\Delta^{4,6}$-cyclohexadiene-1,2-dicarboxylic acid (VII). A mixture of 2.4 g of diester (III) with 20 ml of 15% NaOH solution was boiled for four hours. The solution was filtered and acidified with hydrochloric acid. We obtained 1.55 g of trans-3,4-dimethyl-$\Delta^{4,6}$-cyclohexadiene-1,2-dicarboxylic acid (VII) with m.p. 212-213° (from 40% aqueous acetone, decomposition).

Found %: C 60.84, 60.83; H 5.99, 6.09. $C_{10}H_{12}O_4$. Calculated %: C 61.20; H 6.17.

To obtain the anhydride corresponding to this acid (IX), 0.35 g of acid (VII) was boiled for two hours with 10 ml of acetyl chloride. The solution was evaporated in a vacuum, the crystalline residue was washed with a mixture of ether and ligroin (1 : 1). We obtained 0.2 g of anhydride (IX) with m.p. 95.5-96.5° (from ligroin).

Found %: C 67.19, 66.97; H 5.81, 5.80. $C_{10}H_{10}O_3$. Calculated %: C 67.40; H 5.66.

On treatment of acid (VII) with an ether solution of diazomethane we obtained a quantitative yield of the corresponding diester (VIII) with b.p. 113-114° (4 mm), $n^{18}D$ 1.5080.

Found %: C 63.95, 64.01; H 7.03, 7.09. $C_{12}H_{16}O_4$. Calculated %: C 64.27; H 7.19.

On saponification of this diester with 15% NaOH solution we obtained the starting acid (VII) in good yield.

4. Alkaline saponification of the cis-diester (V). A mixture of 1.8 g of this ester with 20 g of 15% NaOH solution was boiled for three hours. The solution was filtered and acidified with hydrochloric acid to an acid reaction to Congo. The precipitate which formed was filtered off, washed with water, and gave 1.3 g of a mixture of acids with m.p. 160-185° from which crystallization from 40% aqueous acetone gave 0.5 g of trans-3,4-dimethyl-$\Delta^{4,6}$-cyclohexadiene-1,2-dicarboxylic acid (VII) with m.p. 203-206°, not giving a melting point depression with the form described above (see section 3).

5. Ozonization of acid (VII). A stream of ozonized oxygen (amount of ozone 0.45 g/hr) was passed through a solution of 1.5 g of acid (VII) in 90 ml of 95% aqueous acetic acid at 0° for five hours. The ozonide solution was mixed with 10 ml of 70% peracetic acid and the mixture was kept at 40-45° for 16 hr. The acetic and peracetic acids were distilled off in a vacuum, the residue was heated at 150-160° to full cessation of CO_2 evolution, and then was distilled in a vacuum. We obtained 0.3 g of β-methyl levulinic acid (30%), characterized by the semicarbazone with decomposition point 175-176°, not giving a melting point depression with a known sample.

II. 3,5-Dimethyl-$\Delta^{1,4}$-cyclohexadiene-1,2-dicarboxylic Acid (XI), Its Anhydride (X), and Dimethyl Ester (XII)

1. Preparation of anhydride (X), acid (XI), and diester (XII). a) A mixture of 10 g of acetylene dicarboxylic acid, 13 ml of 2-methyl-1,3-pentadiene, 40 ml of dioxane, and 0.2 g of pyrogallol was heated for 23 hr at 65°. The solvent was distilled off in a vacuum and the residue crystallized on cooling. The crystals were pressed free of the tarry oil on the filter and washed with a mixture of ether and ligroin (1 : 1); we obtained 6.1 g of anhydride of 3,5-dimethyl-$\Delta^{1,4}$-cyclohexadiene-1,2-dicarboxylic acid (X) with m.p. 95-96° (from a mixture of ether and ligroin 1 : 2).

Found %: C 67.68, 67.60; H 5.71, 5.77. $C_{10}H_{10}O_3$. Calculated %: C 67.40; H 5.67.

Distillation of the mother liquor in a vacuum gave a further 3.7 g of anhydride (X). Total yield of adduct 9.8 g (62%).

b) For the preparation of acid (XI) 0.55 g of anhydride (X) was dissolved in 5 g of 10% KOH solution. The solution stood overnight, then was filtered and acidified. The crystals which precipitated were filtered off and we obtained 0.5 g of 3,5-dimethyl-$\Delta^{1,4}$-cyclohexadiene-1,2-dicarboxylic acid (XI) with m.p. 121° (decomp.).

Found %: C 61.38, 61.42; H 6.26, 6.17. $C_{10}H_{12}O_4$. Calculated %: C 61.21; H 6.12.

When acid (XI) was boiled for a short time in water solution, it gave anhydride (X) quantitatively.

c) For the preparation of diester (XII) a mixture of 8.9 g of diester of acetylene dicarboxylic acid, 11 g of 2-methyl-1,3-pentadiene, 50 ml of dioxane, and 0.2 g of pyrogallol was heated for six hours at 110-120°. The solvent was distilled off and the residue was distilled in a vacuum. We obtained 12.65 g (90%) of substance with b.p. 114-118° (4 mm), $n^{18.5}D$ 1.4895. Repeated distillations gave 11 g of pure dimethyl ester of 3,5-dimethyl-$\Delta^{1,4}$-cyclohexadiene-1,2-dicarboxylic acid (XII).

B.p. 114.5-116° (4 mm), $n^{20}D$ 1.4898, d^{20}_4 1.102.

Found %: C 64.07, 64.30; H 7.12, 7.14. $C_{12}H_{16}O_4$. Calculated %: C 64.27; H 7.19.

The same diester was obtained quantitatively by treatment of acid (XI) with an ether solution of diazomethane.

2. Alkaline saponification of diester (XII). Trans-3,5-dimethylcyclohexadiene-1,2-dicarboxylic acid (XIV). We boiled 3.6 g of the diester for three hours with 18 g of a 20% KOH solution. The solution was cooled, filtered, and acidified and allowed to stand overnight. The crystals which precipitated were filtered off and washed with water; we obtained 2.45 g of substance with m.p. 155-170°, and after recrystallization of this from 10% aqueous acetone we obtained 1.7 g of 3,5-dimethyl-$\Delta^{4,6}$-cyclohexadiene-1,2-dicarboxylic acid (XIV) with m.p. 180-181° (from acetonitrile, decomposition).

Found %: C 61.52, 61.56; H 6.05, 6.32. $C_{10}H_{12}O_4$. Calculated %: C 61.21; H 6.17.

We boiled 0.5 g of acid (XIV) for one hour with 20 ml of acetyl chloride. The solution was evaporated in a vacuum and the residue was washed on the filter with n-hexane; we obtained 0.37 g of anhydride of 3,5-dimethyl-$\Delta^{4,6}$-cyclohexadiene-1,2-dicarboxylic acid (XVI) with m.p. 98.5-100° (from a mixture of ether and n-hexane, 1 : 1). The product changed when heated to 60°.

3. Alkaline saponification of anhydride (X). Cis-3,6-dimethyl-$\Delta^{4,6}$-cyclohexadiene-1,2-dicarboxylic acid (XIII). Three g of anhydride (X) was added in portions to 30 g of 20% NaOH solution. The resulting suspension was boiled for three hours, then filtered, acidified, and allowed to stand for 12 hr. On standing the mixture separated into a crystalline and a liquid product. The crystals were filtered off and washed with water and with ether; we obtained 1.15 g of a mixture of acids from which after recrystallization from 20% aqueous acetone we separated 0.65 g of cis-3,6-dimethyl-$\Delta^{4,6}$-cyclohexadiene-1,2-dicarboxylic acid (XIII). After drying in a vacuum, it melted at 194-196° (decomp.).

Found %: C 61.35, 61.33; H 6.24, 6.14. $C_{10}H_{12}O_4$. Calculated %: C 61.20; H 6.17.

The wash ether was evaporated dry in a vacuum, the residue (1.8 g with m.p. 95-130°) was dissolved with heat in the wash water and the resulting solution was boiled for 3 min. The crystalline precipitate which separated on cooling was filtered off, washed with water, and gave 0.84 g of a mixture of crystalline substances (A) with m.p. 147-165°. The mixture was boiled for 30 min with 30 ml of n-hexane. The insoluble product (0.45 g) was filtered off and after recrystallization from 20% acetone gave 0.3 g of acid (XIII). From the n-hexane mother liquor we isolated 0.36 g of anhydride (X) with m.p. 87-89°, giving no melting point depression with the form described above. The aqueous mother liquor after separation of mixture (A) was evaporated dry in a vacuum. The residue was boiled with n-hexane and we separated from the insoluble part 0.15 g of 3,5-dimethyl-$\Delta^{1,4}$-cyclohexadiene-1,2-dicarboxylic acid (XI) with m.p. 116°, giving no depression of the melting point with the form described above, and from the filtrate 0.12 g of the anhydride of this acid (X) with m.p. 85-86°, giving no melting point depression with the form described above.

Thus, the products of alkaline saponification of anhydride (X) under standard conditions are the acid (XIII), 0.95 g, and the acid (XI), isolated chiefly in the form of the anhydride (X), 0.6 g.

For obtaining anhydride (XV) 0.5 g of acid (XIII) was boiled for three hours with 10 ml of acetyl chloride. The solution was evaporated dry in a vacuum, the residue was washed on the filter with a mixture of n-hexane and ether (5 : 1), and we obtained 0.32 g of the anhydride of cis-3,5-dimethyl-$\Delta^{4,6}$-cyclohexadiene-1,2-dicarboxylic acid (XV) with m.p. 94-95° (from a mixture of ether and hexane 1 : 1). A sample mixed with anhydrides (X) and (XVI) gave a sharp melting point depression.

Found %: C 67.36, 67.31; H 5.74, 5.69. $C_{10}H_{10}O_3$. Calculated %: C 67.40; H 5.66.

When anhydride (XV) (0.2 g) was boiled with water (2 ml) it was converted quantitatively to acid (XIII).

4. Ozonization of acid (XIII). A stream of oxygen enriched with ozone (amount of ozone 0.55 g/hr) was passed through a solution of 0.9 g of the acid in 70 ml of 95% aqueous acetic acid for six hours. The ozonide solution was mixed with 6 ml of 70% peracetic acid, kept for 20 hr at 45°, and then for a day at 20°. The solvent was distilled off in a vacuum and the residue partly crystallized on standing. The crystals were filtered, washed with a mixture of ether and benzene (1 : 4), and gave 0.25 g of 1,1,2-propane tricarboxylic acid with m.p. 143-144°. A sample mixed with known substance showed no melting point depression. The product was heated at 165-175° to complete cessation of CO_2 evolution (30 min) in a stream of nitrogen. The melt crystallized when cooled. The crystals were carefully washed on the filter with benzene and gave 80 mg of methyl succinic acid with m.p. 108-109°. The sample mixed with known material gave no melting point depression.

III. 4,5-Dimethyl-$\Delta^{1,4}$-cyclohexadiene-1,2-dicarboxylic Acid (XVIII), Its Anhydride (XIX), Its Anhydride (XIX), and Diester (XX) and Their Reactions

1. Preparation of the anhydride (XIX), acid (XVIII), and diester (XX). a) To a solution of 2 g of acetylene dicarboxylic acid in 30 ml of absolute dioxane was added 4 ml of 2,3-dimethylbutadiene and 0.2 g of pyrogallol and the mixture was heated for 15 hr at 65-75°. Dioxane and the excess diene were distilled off in a vacuum and the crystalline residue was washed on the filter with a mixture of ether and ligroin (1 : 1). We obtained 1.55 g of anhydride of 4,5-dimethyl-$\Delta^{1,4}$-cyclohexadiene-1,2-dicarboxylic acid (XIX) with m.p. 168-169° (from a small amount of ether).

Found %: C 67.42, 67.30; H 5.60, 5.70. $C_{10}H_{10}O_3$. Calculated %: C 67.40; H 5.66.

b) For preparation of acid (XVIII) 0.2 g of anhydride (XIX) was shaken with 5 ml of a 10% solution of NaOH. The resulting solution was evaporated in a vacuum to a volume of 1 ml and acidified with hydrochloric acid. The crystals which precipitated were filtered off, washed with cold water, and gave 0.15 g of acid (XVIII) with m.p. 158.5-160.5° (from a small amount of water, decomposition).

Found %: C 60.78, 60.82; H 6.14, 6.32. $C_{10}H_{12}O_4$. Calculated %: C 61.20; H 6.17.

When acid (XVIII) was treated with acetyl chloride it gave a good yield of the starting anhydride (XIX), giving no melting point depression with the form described above.

c) For preparation of diester (XX) a mixture of 5.25 g of dimethyl acetylene dicarboxylate, 9 ml of 2,3-dimethylbutadiene, 70 ml of dioxane, and 0.2 g of pyrogallol were heated six hours in a steel cylinder at 115-120°. Dioxane and excess diene were distilled off and the liquid residue was distilled in a vacuum. We obtained 7.2 g (80%) of dimethyl ester (XX) with b.p. 155-157° (7 mm), which crystallized on standing. M.p. 75-76° (from a mixture of ether and ligroin).

Found %: C 64.30, 64.25; H 7.04, 7.20. $C_{12}H_{16}O_4$. Calculated %: C 64.21, H 7.19.

The same ester with m.p. 75-76° was obtained with a quantitative yield by treatment of acid (XVIII) with an ether solution of diazomethane.

2. Alkaline saponification of diester (XX); 4,5-dimethyl-$\Delta^{4,6}$-cyclohexadiene-1,2-dicarboxylic acid (XXI). A mixture of 2 g of diester (XX) with 30 ml of 15% NaOH solution was boiled for two hours. The solution was filtered and acidified to Congo with hydrochloric acid. The crystals which precipitated were filtered off, washed with water, and dried in air. We obtained 1.4 g (80%) of 4,5-dimethyl-$\Delta^{2,4}$-cyclohexadiene-1,2-dicarboxylic acid (XXI) with m.p. 202.5-204.5° (from 20% aqueous acetone, decomposition).

Found %: C 60.94, 60.94; H 6.29, 6.20. $C_{10}H_{12}O_4$. Calculated %: C 61.20; H 6.17.

When 0.4 g of acid (XXI) was boiled for three hours with 15 ml of acetyl chloride, followed by treatment analogous to that described above, we obtained 0.35 g of anhydride (XXII) with m.p. 133-134° (from a mixture of ether and ligroin).

Found %: C 67.20, 66.94; H 5.67, 5.68. $C_{10}H_{10}O_3$. Calculated %: C 67.40; H 5.66.

Boiling acid (XXI) with acetic anhydride for two hours gave a quantitative yield of anhydride (XIX) with m.p. 168-169°.

Saponification of anhydride (XXII) by boiling with 20% aqueous acetone gave the starting acid (XXI) quantitatively with m.p. 202-203° (decomp.), giving no melting point depression with the form described above.

To obtain the diester (XXIII) we treated a solution of 1.4 g of acid (XXI) in methanol with an ether solution of diazomethane. After distillation of the solvent the liquid residue was distilled in a vacuum and gave 1.4 g of diester (XXIII) with b.p. 148-149° (10 mm), $n^{20}D$ 1.5130.

Found %: C 64.21, 64.00, H 7.26, 7.20. $C_{12}H_{11}O_4$. Calculated %: C 64.27; H 7.19.

Saponification of this ester with a 20% NaOH solution gave a good yield of the starting acid (XXI) with m.p. 202-204° (decomp.), not giving a melting point depression with the form described above.

3. Alkaline saponification of anhydride (XIX). A mixture of 1 g of anhydride (XIX) with 5 ml of 20% NaOH solution was boiled for three hours. The solution was filtered, acidified with hydrochloric acid, and allowed to stand for three hours. The crystals which precipitated were filtered off, washed with water, and dried in air. We obtained 0.7 g of 4,5-dimethyl-$\Delta^{2,4}$-cyclohexadiene-1,2-dicarboxylic acid (XXI) with m.p. 197-199°. A sample mixed with the form described above gave no melting point depression.

IV. 3,6-Dimethyl-$\Delta^{1,4}$-cyclohexadiene-1,2-dicarboxylic Acid (XXIV), Its Anhydride (XXV), and Diester (XXVI) and Their Reactions

1. Obtaining anhydride (XXV), acid (XXIV), and diester (XXVI). a) A mixture of 8 g of acetylene dicarboxylic acid, 15 ml of 2,6-hexadiene, 80 ml of benzene, 10 ml of acetone, and 0.2 g of pyrogallol was boiled for 24.5 hr. The temperature of the reaction mixture was 72°. The solution was cooled, the benzene layer was separated and evaporated in a vacuum. The residue crystallized. The crystals were pressed and washed on the filter with a mixture of ether and ligroin (4 : 1); we obtained 6.15 g of crude anhydride (XXV). For purification, the ether solution of the reaction product was passed through a layer of aluminum oxide (10 g) and we obtained 5.65 g (45%) of the anhydride of 3,6-dimethyl-$\Delta^{1,4}$-cyclohexadiene-1,2-carboxylic acid (XXV) with m.p. 80-81.5° (from ligroin).

Found %: C 67.65, 67.65; H 5.54, 5.68. $C_{10}H_{10}O_3$. Calculated %: C 67.40; H 5.66.

b) For the preparation of acid (XXIV) 0.5 g of the anhydride (XXV) was dissolved in 5 g of 10% NaOH solution and allowed to stand at room temperature for 64 hr. The solution was filtered, acidified, and the crystals which separated in an acid medium were filtered off and washed with water; we obtained 0.4 g of 3,6-dimethyl-$\Delta^{1,4}$-cyclohexadiene-1,2-dicarboxylic acid (XXIV) with m.p. 115° (from a mixture of benzene and ether 1 : 1). When this acid was boiled for 5 min in a water solution, a quantitative yield of anhydride (XXV) was obtained. Drying acid (XXIV) in a vacuum at room temperature was also accompanied by anhydride formation.

c) For preparation of the diester (XXVI), 2 g of anhydride (XXV) was boiled for 11 hr with 20 ml of methanol. The solution was evaporated to a volume of 5 ml and treated with an ether solution of diazomethane. The solvent was distilled off and the residue was distilled in a vacuum. We obtained 2 g of dimethyl ester of 3,6-dimethyl-$\Delta^{1,4}$-cyclohexadiene-1,2-dicarboxylic acid (XXVI) with b.p. 102.5-103° (3 mm), $n^{17.5}D$ 1.4855.

Found %: C 63.96, 64.01; H 7.21, 7.19. $C_{12}H_{16}O_4$. Calculated %: C 64.27; H 7.19.

The same ester was obtained with a yield of 70% by diene condensation of 10 g of dimethyl acetylene dicarboxylate with 9.8 g of 2,4-hexadiene in 56 ml of dioxane in the presence of pyrogallol.

2. Alkaline saponification of diester (XXVI). Trans-3,6-dimethyl-$\Delta^{4,6}$- cyclohexadiene-1,2-dicarboxylic acid (XXVIII). Two g of diester was boiled for three hours with 10 g of 20% KOH solution. The solution was filtered, acidified, and allowed to stand overnight. The crystals which precipitated were filtered off, washed with water, and several times with ether. We obtained 0.43 g of substance with m.p. 163-165°, from which by recrystallization in 30% aqueous acetone we separated 0.32 g of 3,6-dimethyl- $\Delta^{4,6}$ -cyclohexadiene-1,2-dicarboxylic acid with m.p. 173-174° (decomp.). After drying in a vacuum to constant weight, m.p. 178-180° (decomp.).

Found %: C 60.90, 60.79; H 6.05, 5.97. $C_{10}H_{12}O_4$. Calculated %: C 61.21; H 6.17.

The wash ether solution was evaporated dry in a vacuum, the residue (0.55 g with m.p. 73-130°) was dissolved in the wash water and boiled for three minutes. The oil which precipitated in the boiling solution crystallized on cooling; we obtained 0.57 g of a mixture of crystalline substances with m.p. 75-100°, from which extraction with n-hexane separated 0.44 g of anhydride of 3,6-dimethyl-$\Delta^{1,4}$-cyclohexadiene-1,2-dicarboxylic acid (XXV), giving no depression of the melting point with the form described above. The portion insoluble in n-hexane was recrystallized from 30% acetone and gave a further 0.12 g of acid (XXVIII).

For preparation of anhydride (XXX) 0.9 g of acid (XXVIII) was boiled for one hour with 15 ml of acetyl chloride. The solution was evaporated dry in a vacuum, the residue was washed on the filter with ligroin, and gave 0.75 g of anhydride of 3,6-dimethyl-$\Delta^{4,6}$-cyclohexadiene-1,2-dicarboxylic acid (XXX) with m.p. 117-118° (from a mixture of ether and ligroin).

Found %: C 67.61, 67.41; H 5.80, 5.73. $C_{10}H_{10}O_3$. Calculated %: C 67.40; H 5.66.

When anhydride (XXX) was boiled for 10 min in water solution it formed the above described acid (XXVIII) quantitatively.

3. Alkaline saponification of anhydride (XXV). Cis-3,6-dimethyl-$\Delta^{4,6}$-cyclohexadiene-1,2-dicarboxylic acid (XXVII). We dissolved 3.55 g of anhydride (XXV) in 36.5 g of 20% KOH solution. The solution was boiled for three hours then cooled, filtered, acidified, and allowed to stand overnight. The crystals which precipitated were filtered off, washed with water and then with ether, and gave 2 g of substance with m.p. 155-165° (a). The wash ether solution was evaporated dry in a vacuum and gave 0.8 g of substance with m.p. 90-100° (b).

Recrystallization of fraction "a" from 40% aqueous acetone gave 0.5 g of cis-3,6-dimethyl-$\Delta^{4,6}$-cyclohexadiene-1,2-dicarboxylic acid (XXVII) with m.p. 180-181°. After drying in a vacuum over $CaCl_2$ this acid had m.p. 205-206° (decomp.).

Found %: C 61.56, 61.33; H 6.19, 6.10. $C_{10}H_{12}O_4$. Calculated %: C 61.21; H 6.17.

The mother water-acetone liquors were evaporated in a vacuum, the residues were combined with fraction "b" and were extracted with boiling ligroin. The insoluble residue (1.15 g) was filtered off and after recrystallization from 40% aqueous acetone gave a further 0.6 g of acid (XXVII). The filtrate was evaporated to a volume of 6 ml; on standing 1.04 g of anhydride of 3,6-dimethyl-$\Delta^{1,4}$-cyclohexadiene-1,2-dicarboxylic acid with m.p. 78-80° crystallized. A mixed sample with the form described above gave no melting point depression.

Ten hour boiling of anhydride (XXV) with 20% KOH solution gave only a mixture of isomeric acids (XXVII) and (XXVIII).

For preparation of the anhydride (XXIX) 0.3 g of acid (XXVII) was boiled for 4.5 hr with 10 ml of acetyl chloride. The solution was evaporated dry in a vacuum, the residue was washed on the filter with a mixture of ether and ligroin (1 : 2) and gave 0.15 g of anhydride (XXIX) with m.p. 86-87.5°.

Found %: C 67.67, 67.64; H 5.77, 5.64. $C_{10}H_{10}O_3$. Calculated %: C 67.40; H 5.06.

4. Ozonization of acid (XXVII). A stream of oxygen enriched with ozone (amount of ozone 0.52 g/ hr) was passed into a solution of 1.5 g of acid in 70 ml of 95% aqueous acetic acid for six hours. The reaction mixture was treated with 10 ml of 70% peracetic acid and kept for 17 hr at 45° and then for 24 hr at 20°. The solvent was distilled off in a vacuum, the crystalline residue was washed on the filter with a mixture of benzene and ether (3 : 2), and gave 0.75 g of 1,1,2-propane tricarboxylic acid with m.p. 135-137°. From the wash solution we isolated a further 0.12 g of the same product. The total yield of 1,1,2-propane tricarboxylic acid was 64.5% with m.p. 154° (from a mixture of benzene and ether 5 : 1, decomposition), which agreed with the literature value [3]. We heated 0.3 g of 1,1,2-propane tricarboxylic acid at 170-175° in a stream of nitrogen to complete cessation of evolution of CO_2 (20 min). When cooled, the melt crystallized, the crystals were washed on the filter with benzene, and we obtained 0.1 g of methyl succinic acid with m.p. 109-111°, not giving a melting point depression with a known sample.

SUMMARY

1. By study of the alkaline isomerization of derivatives of dimethyl-$\Delta^{1,4}$-cyclohexadiene-1,2-dicarboxylic acid it was shown that in the case of the acids 3,4-dimethyl-$\Delta^{1,4}$-cyclohexadiene-1,2-dicarboxylic acid, 3,5-dimethyl-$\Delta^{1,4}$-cyclohexadiene-1,2-dicarboxylic acid, and 4,5-dimethyl-$\Delta^{1,4}$-cyclohexadiene-1,2-dicarboxylic acid there is a shift of the Δ^1-double bond only to the unsubstituted Δ^6-position.

2. It has been shown that in these cases, when as a result of rearrangement of the Δ^1-double bond there can be formation of a new center of asymmetry, there are formed geometric isomers of the corresponding dicarboxylic acids which contain a system of conjugated double bonds.

3. In the case of 3,6-dimethyl-$\Delta^{1,4}$-cyclohexadiene-1,2-dicarboxylic acid it has been shown that the shift of the Δ^1-double bond is also possible in the substituted Δ^6-position, but the shift of the Δ^4-double bond does not occur here.

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All abbreviations of periodicals in the above bibliography are letter-by-letter transliterations of the abbreviations as given in the original Russian journal. *Some or all of this periodical literature may well be available in English translation.* A complete list of the cover-to-cover English translations appears at the back of this issue.

STUDIES OF CHITIN

IV. PREPARATION AND PROPERTIES OF CARBOXYMETHYL CHITIN

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The literature contains descriptions of hydrophilic esters of chitin: chitin sulfate [1], hydroethyl [2] and glyceryl esters [3]. There are indications in the patent literature that water soluble salts of carboxymethyl chitin (CMC) and carboxyethyl chitin (CEC) can be obtained by treatment of alkaline chitin with the corresponding monochloroacetic or α-chloropropionic acids [4]. Water soluble salts of chitin sulfate, CMC, and CEC [5] can be used as boring substances, and as pastes for other purposes. Recently carboxymethylated chitins have been studied by Okimasu [6].

As our studies have shown, CMC can be obtained under mild conditions without splitting of the acetyl groups from the amino groups and it is possible to decrease the destruction of the chitin macromolecule. It is interesting to compare the properties of CMC and carboxymethylcellulose (CMCe) [7], which is widely used in various branches of industry.

Preparations of CMC soluble in water can serve for determination of diameter and form of the macromolecules of chitin derivatives in solution.

EXPERIMENTAL*

For preparing CMC we have used finely ground chitin sifted through a 0.25 mm sieve which was first treated with an alkaline solution in two ways: 1) by soaking in excess alkali with a bath coefficient 1 : 10 for 24 hr at room temperature followed by pressing out to three times the weight; 2) by treatment with the required amount of alkali at room temperature for three hours.

Preliminary experiments established that when monochloroacetic acid acts on alkali chitin (obtained by treatment with a 20-33% solution of sodium hydroxide), the corresponding chitin derivative soluble in water or dilute alkali solutions is not obtained. Therefore, afterwards we used a 40-50% sodium hydroxide solution for preparing alkaline chitin.

Alkaline chitin was treated with the calculated amount of monochloroacetic acid (MCA) and the reaction was carried out at 20, 40, and 60° for 12-20 hr in a flask with a stirrer. At the end of this time the contents of the flask were transferred to a beaker and water was added. Strong swelling and solution of the mass occurred. For purification from alkali and salts the synthesized substance was precipitated with methyl alcohol and washed to a negative reaction for alkalinity. The final washing out of salts was carried out with 80% methyl alcohol in a Soxhlet apparatus to negative reaction for chloride ion. The purified CMC as the sodium salt was separated by water into soluble and insoluble portions. The water soluble part of the CMC was precipitated by methyl alcohol, washed 3-4 times with acetone, and dried to constant weight at 60°. The insoluble portion of the CMC, strongly swelled, was dehydrated with methyl alcohol, acetone, and was also dried at 60°.

Table 1 gives the conditions for preparing CMC.

Table 1 shows that increase in reaction temperature results in decreased percent of reacting chitin, but is not reflected in degree of substitution. Increased reaction temperature causes destruction of the chitin macromolecule, which is indicated by the decrease in viscosity of the 1% solution in water of the different forms.

*With participation of S. S. Karpova and F. G. Khavkina.

TABLE 1. Conditions for Synthesis of Carboxymethyl Chitin and Its Properties

No.	Moles NaOH and MCA per mole chitin		Temp.	Chitin used (in g)	Reacting chitin (%)	Na content (in %)		Degree of substitution of soluble part	Viscosity of 1% water solution (centipoises)
	NaOH	MCA				soluble part	insoluble part		
1	6	3	20°	1.5	82.6	7.30	—	0.89	35.57
2			40	4.0	69.0	7.51	3.58	0.92	30.18
3			60	4.0	40.0	7.16	3.12	0.88	24.10
4	4	2	20	2.0	57.5	6.89	3.70	0.84	16.63
5			40	4.0	68.5	6.91	3.25	0.84	12.64
6			60	4.0	40.7	6.44	2.63	0.79	7.41
7	12	9	20	2.0	45.0	6.62	0.16	0.81	—
8			40	4.0	30.0	5.45	0.52	0.67	—
9			60	4.0	28.2	—	0.19	—	—
10	6	3	20	2.0	93.0	7.93	3.52	0.97	22.18
11			40	7.0	76.0	8.76	2.62	1.08	11.13
12			60	7.0	60.0	7.21	3.76	0.88	26.06
13	4	2	20	2.0	63.0	8.56	2.05	1.05	14.76
14			40	4.0	57.0	6.98	2.35	0.85	5.74
15			60	4.0	18.7	7.04	2.10	0.86	4.58

Note: The NaOH concentration in Expts. 1-6 was 40%; in Expts. 7-15, 49.25%. Duration of experiments, 20 hr.

If chitin is treated with excess alkali solution with later pressing out, then on treatment with monochloroacetic acid there is some increase in percent of reacting chitin after less time of reaction even at increased temperature (see Table 2).

However, the use of chitin treated with the calculated amount of alkali for three hours has the advantage that here there is a decrease in time of steeping; the amount of alkali is less and at the same time it is possible to obtain CMC with a maximum yield in the esterification of chitin at room temperature. For a study of the samples we determined the degree of substitution by the method of calcination. Analysis of the CMC sodium salt for free amino groups by the Van Slyke method gave negative results.

Carboxymethyl chitin is a hygroscopic substance and at room temperature under laboratory conditions contains 16.60% moisture. If it is kept in a desiccator over water (with 100% relative humidity) it absorbs 106-108% moisture and equilibrium is reached after 18-20 days.

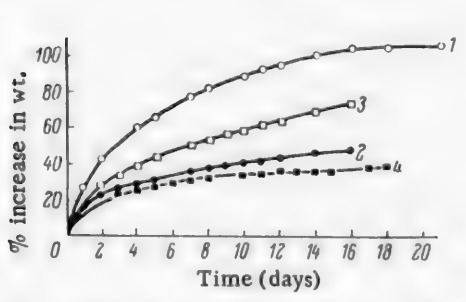

Fig. 1. Increase in weight with time. 1) CMC; 2) chitin glycolic acid, degree of substitution 0.88; 3) CMCe; 4) cellulose glycolic acid with degree of substitution 0.76.

By acidification of the Na salt of CMC with dilute hydrochloric acid at room temperature, followed by washing with methyl alcohol to negative reaction for chloride, we obtained chitin glycolic acid. In distinction from cellulose glycolic acid, which we obtained from the industrial form of CMCe (degree of substitution 0.76), the chitin glycolic acid (degree of substitution 0.88) swelled strongly and partly dissolved in water. In a study of its hygroscopic character at 100% relative humidity we showed that the glycolic acid of chitin hygroscopicity was more than that of cellulose glycolic acid, as Fig. 1 shows.

Analysis of chitin glycolic acid for primary amino groups also gave negative results, which indicates that the acetamide groups are retained in the molecule.

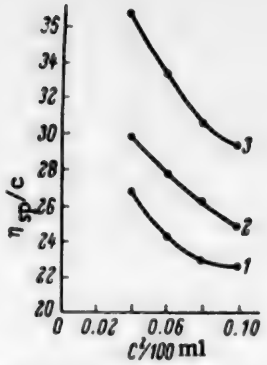

Fig. 2. Relation of η_{sp}/c to c for samples of CMC in water at 20°. 1) Degree of substitution 0.97 (viscosity 22.18 centipoises); 2) degree of substitution 0.88 (viscosity 22.84 centipoises) 3) degree of substitution 0.88 (viscosity 26.06 centipoises).

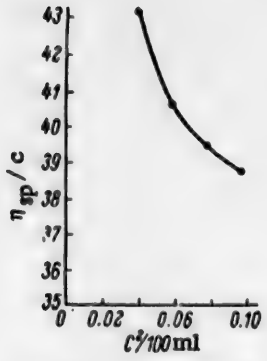

Fig. 3. Relation of η_{sp}/c to c for CMCe, Degree of substitution 0.76 (viscosity 69.20 centipoises) in water at 20°.

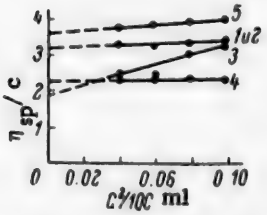

Fig. 4. Relation of η_{sp}/c to c for samples of CMC and CMCe in 6% NaOH at 20°. 1) Sample 12; 2) sample 10; 3) sample 3 (Table 2); 4) sample 11; 5) sample of CMCe.

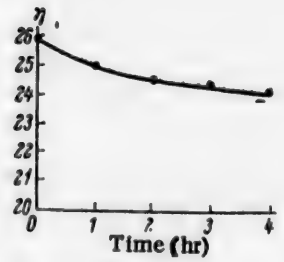

Fig. 5. Change in viscosity of a 1% aqueous solution of CMCe at 50° with time.

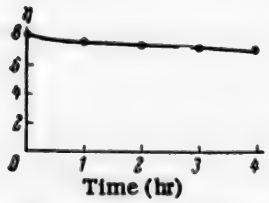

Fig. 6. Change in viscosity of a 1% aqueous solution of CMC (sample 11) at 50° with time (Table 1).

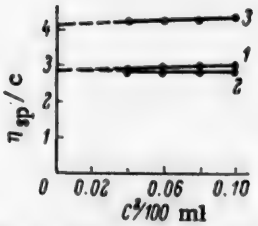

Fig. 7. Relation of η_{sp}/c to c for regenerated samples (after heating at 50° for 4 hr) in 6% NaOH at 20°. 1) Form 11 (Table 1); 2) form 10 (Table 1); 3) CMCe.

TABLE 2. Conditions for Synthesis of Carboxymethyl Chitin and Its Properties

No.	NaOH concentration, %	Time (hr)	Temp.	Chitin taken, g	Reacting chitin, %	Na Content, %		Degree of substitution of soluble part	Viscosity of 1% water solution, centipoises
						soluble part	insoluble part		
1	50.15	14.0	40°	5.2	85.5	6.88	4.10	0.84	40.43
2	49.76	18.5	60	3.0	87.3	7.32	4.13	0.89	37.19
3	49.76	18.5	40	3.4	88.2	7.25	3.91	0.88	22.84
4	49.76	12.0	60	2.7	88.8	6.13	2.30	0.75	30.20

Note: In all the experiments the ratio of moles NaOH per 1 mole of chitin was 6, and the ratio of moles of MCA per mole of chitin was 3.

Carboxymethyl chitin containing 6.13% Na or more dissolves well in water. Heating the water solution does not cause coagulation, just as in the case of carboxymethylcellulose. In the study of dilute water solutions of CMC it was shown that their properties are analogous to those of dilute aqueous solutions of CMCe, that is, with dilution of the solution there is an increase in specific viscosity, as Figs. 2 and 3 show.

Thus, the solution of CMC is a polyelectrolyte. In order to remove the polyelectrolyte effect we added alkali to the solution and determined the characteristic viscosity in alkali solution [8]. We measured the characteristic viscosity in 6% sodium hydroxide solution (see Fig. 4).

From a comparison of the characteristic viscosities we see that for sample 3 (curve 3) it is less than for the other samples, which is directly connected with the conditions of preparing both the alkaline chitin and the carboxymethyl chitin.

When we measured the viscosity of a 1% aqueous solution of CMC and CMCe at 50° with time, we showed that there is a gradual fall in viscosity, as Figs. 5 and 6 show.

For CMCe the fall in viscosity after 4 hr heating is 1.66, and for CMC 0.64 centipoises.

For an explanation of the reason for the fall in viscosity the samples were regenerated from the solution after heating and we determined their characteristic viscosity and chemical composition. The chemical composition was not changed, but the characteristic viscosity, except for sample 10 (curve 2, Fig. 7), even increased slightly. Evidently we did not succed in precipitating the low molecular portion of these samples, so that there was a rise in characteristic viscosity. The fall in viscosity of 1% solutions is obviously connected with decreasing molecular weight.

SUMMARY

1. We have shown that the best conditions for obtaining carboxymethyl chitin are treatment of alkaline chitin (obtained by the action of 6 moles of 49.25% NaOH solution on 1 mole of chitin for three hours) with monochloroacetic acid (3 moles) at room temperature for 20 hr. This causes no hydrolysis of acetyl on the amino nitrogen.

2. We have studied the properties of aqueous solutions of carboxymethyl chitin and determined the characteristic viscosities in 6% NaOH.

3. We have shown that the hygroscopicity of carboxymethyl chitin and chitin glycolic acid at 100% relative humidity is greater than the corresponding hygroscopicity of carboxymethyl cellulose and cellulose glycolic acid.

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SYNTHESIS OF CELLULOSE ETHERS WITH THE HELP OF ESTERS OF BENZENESULFONIC ACID. II*

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Original article submitted May 11, 1960

In the preceding paper [1] it was shown that esters of sulfonic acids can be used as agents for the alkylation of cellulose if the latter is previously dissolved in triethylbenzylammonium hydroxide or 9-10% sodium hydroxide solution. It was found that cellulose alkylation in sodium hydroxide solution goes more slowly when the alkylating agents contain long alkyl groups. This difference is not observed when the same esters are used for alkylation of cellulose in a solution of an organic base. In the latter the reaction goes at the same speed in each case.

It was therefore of interest to investigate esters of benzenesulfonic acid containing alkyl residues of higher aliphatic alcohols. We hoped in this way to obtain unknown ethers of cellulose that would be difficult to prepare with the help of alkyl halides. The synthesis of hexylcellulose from hexyl chloride and alkali cellulose was previously described [2], but films formed from this hexylcellulose had low mechanical strength [3] due to the drastic conditions of synthesis.

Our experiments showed that alkylation of cellulose by esters of benzenesulfonic acid makes possible the preparation of less degraded cellulose ethers.

EXPERIMENTAL**

Benzenesulfonic acid esters were prepared by a modification of the method of V. A. Izmail'skii and B. A. Razorenov [4]. To 1 mole of benzenesulfochloride was added 0.9 mole of the appropriate normal alcohol (hexyl, heptyl, octyl, nonyl, or decyl), and dropwise addition was then made of 1.12 moles of 40% sodium hydroxide in the course of an hour. The reaction was continued for another 1-3 hr at 10-15° or at 40°. The ester was then washed free of salts and alkali with water, and dried with potassium carbonate prior to distillation in vacuo.

In Table 1 are set forth the conditions of preparation and properties of sulfonic acid esters prepared for the first time.

Hexyl, heptyl, octyl, nonyl, and decyl esters of benzenesulfonic acid are high-boiling, colorless liquids, readily miscible with organic solvents.

The prepared esters of benzenesulfonic acid served as starting substances for cellulose ethers. Cellulose was previously dissolved in the organic base (12 moles) to form a 2.3% cellulose solution, and the solution was then heated to 70°; the benzenesulfonic ester was added at this temperature, and the contents of the flask were stirred for 2 hr. The resulting cellulose ethers were afterwards purified by the usual treatment. The properties of the ethers are set forth in Table 2, from which we see that with increasing quantity of alkylating agent the degree of substitution increases and the viscosity decreases.

For octyl- and nonylcellulose the highest degree of substitution occurs on etherification with six moles of the appropriate benzenesulfonic acid ester. Further increase in the quantity of alkylating agent does not lead to an increase in the degree of substitution.

Depending on the degree of substitution, cellulose ethers are soluble in pyridine, piperidine, and alcohol-benzene mixture. A second alkylation of the cellulose ethers did not lead to an appreciable increase in degree of substitution.

* For I see [1].

** With participation of S. S. Karpova and F. G. Khavkina.

TABLE 1. Conditions of Preparation and Properties of Sulfonic Acid Esters

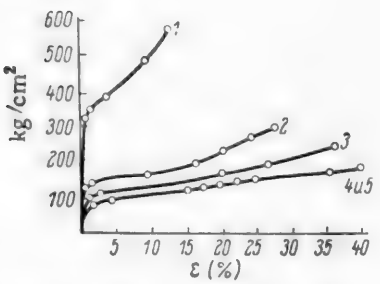
Sulfonic acid ester	Reaction temp.	Duration (hr)	Yield, (%)	Boiling point (pressure in mm)	n_D^{20}	d_4^{20}
$C_6H_5SO_2—O(CH_2)_5CH_3$	10—15°	2	46.20	156—159° (2)	1.4965	1.1005
$C_6H_5SO_2—O(CH_2)_6CH_3$	40	4	43.40	161—163 (2)	1.4937	1.0869
$C_6H_5SO_2—O(CH_2)_7CH_3$	10—15	4	49.73	165—167 (2)	1.4912	1.0663
$C_6H_5SO_2—O(CH_2)_8CH_3$	10—15	4	49.94	175—179 (0.5)	1.4909	1.0571
$C_6H_5SO_2—O(CH_2)_9CH_3$	40	4	49.88	185—187 (0.5)	1.4868	1.0352

TABLE 2. Properties of Cellulose Ethers

Prep. no.	Cellulose ether	No. of moles of BSA ester per mole of cellulose	Melting point	% C	% H	Degree of substitution	Viscosity of 1% solution (centipoises)	[η]
1	Hexyl	6	238°	61.27	9.34	1.29	6.08	2.7
2	Hexyl	8	232	62.82	9.42	1.48	4.63	2.0
3	Hexyl	10	229	64.29	10.03	1.76	3.72	1.8
4	Heptyl	3	—	56.83	9.36	0.76	—	2.10
5	Heptyl	6	217	64.30	10.45	1.55	10.08	1.90
6	Heptyl	8	215	67.73	10.92	1.82	6.39	3.10
7	Octyl	6	200	68.54	11.25	2.09	13.84	2.20
8	Octyl	8	197	67.92	11.11	1.92	6.31	1.75
9	Octyl	10	196	68.57	11.22	2.07	4.71	1.30
10	Nonyl	6	196	69.64	11.25	2.03	14.41	3.65
11	Nonyl	8	200	70.08	11.28	2.09	—	2.65
12	Nonyl	10	198	68.63	11.29	1.85	6.63	2.30
13	Decyl	6	198	67.30	10.56	1.50	3.55	1.35
14	Decyl	8	198	69.51	10.57	1.70	3.66	1.15
15	Decyl	10	198	70.03	11.20	1.88	3.75	1.32

Films of all of the prepared cellulose ethers were run onto glass or mercury. After prolonged drying in a vacuum-desiccator at 40° to constant weight, the films were tested for mechanical strength in a tensile testing apparatus.

Load–elongation curves of specimens of cellulose ethers prepared under identical conditions are plotted in the figure.



Load–elongation curves. 1) Hexylcellulose 1.50; 2) heptylcellulose 1.82; 3) octylcellulose 1.92; 4) nonylcellulose 2.09; 5) decylcellulose 1.70. (The numbers are degrees of substitution).

The figure indicates that the hexylcellulose film is stronger than the decylcellulose film, but its elongation is lower. In respect to mechanical strength heptylcellulose is intermediate between hexyl- and decylcelluloses.

The new ethers are water-repellent substances and absorb little moisture. The water uptake of specimens is inversely proportional to the degree of substitution; also the higher the position of the alkyl radical in the homologous series, the lower is the water uptake.

SUMMARY

1. The hexyl, heptyl, octyl, nonyl, and decyl esters of benzenesulfonic acid were prepared for the first time and characterized.

2. These esters are alkylating agents that enable the synthesis of new ethers of cellulose which are soluble in pyridine, piperidine or a mixture of alcohol and benzene depending on the degree of substitution.

3. Films were prepared from hexyl-, heptyl-, octyl-, nonyl-, and decylcelluloses and examined for their mechanical strength. It was shown that hexylcellulose films are as strong as ethylcellulose films and considerably stronger than nonyl- and decylcellulose films.

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REACTION OF MERCURY SALTS WITH SECONDARY – TERTIARY α-GLYCOLS OF THE ACETYLENIC SERIES

IV. 1,2,4-TRIPHENYL-3-BUTYNE-1,2-DIOL, 3-METHYL-5-PHENYL-4-PENTYNE-2,3-DIOL AND MERCURIC CHLORIDE

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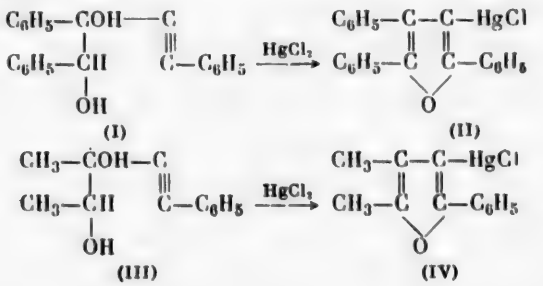
É. D. Venus-Danilova and V. M. Al'bitskaya earlier established that substituted furans are formed in good yields when mercuric chloride acts on 1,2,4-triphenyl-3-butyne-1,2-diol and 3-methyl-5-phenyl-4-pentyne-2,3-diol [1, 2].

Further investigations by Venus-Danilova and one of us [3-5] led to clarification of the role of mercury salts and to a considerable simplification of the conditions of this reaction. Intermediate products were isolated in the shape of β-chloromercurifurans. The reaction of secondary–tertiary α-glycols of the acetylenic series can therefore serve not only as a convenient route to substituted furans, but also for the preparation of β-chloromercurifurans with an unsubstituted α-position [4], which formerly were not easily accessible.

We proposed a general scheme for interaction of mercury salts with the above glycols in one of our earlier communications [3].

In their work on reaction of mercuric chloride with 1,2,4-triphenyl-3-butyne-1,2-diol and with 3-methyl-5-phenyl-4-pentyne-2,3-diol, Venus-Danilova and Al'bitskaya [1, 2] isolated only the endproducts of the reaction and did not detect the choromercuri- compounds. It was therefore of interest to investigate whether it was also possible in the case of these glycols to isolate the substituted chloromercurifurans in good yields. We also required these compounds for other purposes.

Our experiments showed that chloromercurifurans (II and (IV) are also formed in this case. It must be noted, however, that the formation of organomercury compounds from 1,2,4-triphenyl-3-butyne-1,2-diol goes very much more slowly than from all glycols investigated earlier. However even in the cold the reaction started in the course of a minute and the mass quickly thickened due to formation of the chloromercurifuran. A somewhat slower, but still fairly fast reaction was also observed earlier in the case of 5,5-dimethyl-1,2-diphenyl-3-hexyne-1,2-diol which differs from glycol (I) only by the presence of a tert butyl group in place of phenyl at the acetylenic carbon. This behavior was explained by the steric hindrance of the tert butyl residue [5]. There is probably another cause for the slower reaction of the glycol, since 1,2,4-triphenyl-3-butyne-1,2-diol reacts with mercuric chloride only after heating for 20 min at 45°.



(I) (II) (III) (IV)

On using acetone as solvent instead of alcohol, we found that the β-chloromercurifurans (II and IV) did not separate out, but when solutions of the glycol and mercuric chloride were allowed to stand for several days at room temperature the corresponding substituted furans were at once obtained. A possible explanation of this phenomenon is that β-chloromercurifurans are very much more easily soluble in acetone than in alcohol and remain in solution, and their conversion into furans goes very much more quickly in solution than in the solid state.

EXPERIMENTAL

1,2,4-Triphenyl-3-butyne-1,2-diol (I)

Preparation of 1,2,4-triphenyl-3-butyne-1,2-diol. We slightly modified the method of preparation of the glycol described in the literature [6] and were thus able to increase the yield to 77.7% (from 63%) calculated on the benzoin taken.

To an ethereal solution of phenylacetylenemagnesium bromide, prepared in the usual manner from 25 g of magnesium, was added 53 g of benzoin (20 g in solution in 500 ml of anhydrous benzene and the remaining 33 g in the form of a fine powder). The reaction mass was heated for 2 hr at 45° and left overnight at room temperature. The next day the mass was decomposed with dilute hydrochloric acid, and the ether–benzene layer was washed with sodium carbonate solution and dried with anhydrous sodium sulfate. During this treatment some of the glycol came out of solution and had to be filtered hot from the sodium sulfate. The solid substance isolated after cooling of the filtered solution weighed 59 g. Distillation of the ether and benzene from the solution gave another 29.5 g of crude glycol, which was purified by washing with ligroin. The mother liquor and the ligroin were combined and the phenylacetylene recovered therefrom by distillation.

Recrystallization from alcohol gave 61 g of pure glycol with m.p. 174-175°.

Action of mercuric chloride on 1,2,4-triphenyl-3-butyne-1,2-diol. a) A solution of 5 g of the glycol in 75 ml of boiling alcohol was cooled to 45°, and a solution of 4.3 g of mercuric chloride in 25 ml of alcohol was then added. Crystals commenced to come down after 20 min, and the quantity of precipitate increased very slowly. After 8 hr the crystals were filtered and washed with alcohol. There was obtained 6.1 g of substance with m.p. 192-193° (from a 1 : 3 mixture of dioxane and acetone). The substance does not contain hydroxyl or carbonyl groups, and judging by the analysis it is 2,3,5-triphenyl-4-chloromercurifuran (II), which has not been described in the literature.

Found %: Hg 37.69, 37.81; Cl 6.65, 6.61. $C_{22}H_{15}OHgCl$. Calculated %: Hg 37.77; Cl 6.68.

The molecular weight is not reported since unsatisfactory results were obtained due to the poor solubility.

b) A solution of 5 g of the glycol in 35 ml of acetone and 4.3 g of mercuric chloride dissolved in 15 ml of acetone were run together. No precipitate appeared after standing at the ordinary temperature for four days. The solution was poured into 300 ml of water. An oil came down and quickly crystallized. The product was washed with water and dried to give 3.6 g (76.4%) of 2,3,5-triphenylfuran with m.p. 90-91° (from alcohol) [1, 7].

3-Methyl-5-phenyl-4-pentyne-2,3-diol (III)

Synthesis of the glycol. It was prepared by the literature method [3] from phenylacetylenemagnesium bromide and acetone in a yield of 49.4%. The synthesis gave only the low-melting form of the glycol with m.p. 54-55°.

Action of mercuric chloride on 3-methyl-5-phenyl-4-pentyne-2,3-diol. a) Glycol (5 g) and mercuric chloride (7.5 g) were separately dissolved in a total volume of 60 ml of alcohol. After the cold solutions had been run together, crystals began to separate after only one minute, and the entire mass quickly solidified. After 2 hr the precipitate was filtered. There was obtained 6.2 g of substance with m.p. 177-178° (from alcohol). It does not react either with methylmagnesium iodide or with 2,4-dinitrophenylhydrazine.

Found %: Hg 49.07, 49.19; Cl 8.64, 8.63. M 412 (acc. Rast). $C_{12}H_{11}OHgCl$. Calculated %: Hg 49.27; Cl 8.72. M 407.1.

Judging by the analytical data and the properties, the substance is 2,3-dimethyl-5-phenyl-4-chloromercurifuran (IV), which has not been described previously.

b) Glycol (5 g) was dissolved in 35 ml of acetone and mercuric chloride (7.2 g) in 15 ml of acetone. No precipitate appeared when the two solutions were run together. On the fourth day the reaction mixture was poured

into 300 ml of water. An oil came out and was extracted with benzene. The extract was dried, the benzene distilled off, and the residual oil distilled in vacuo to give 3.9 g (86%) of greenish liquid with b.p. 108-112° (4 mm). The product gave negative reactions for hydroxyl and carbonyl groups. It is 2,3-dimethyl-5-phenylfuran [2, 8].

SUMMARY

1. It was shown that formation of substituted furans from 1,2,4-triphenyl-3-butyne-1,2-diol and 3-methyl-5-phenyl-4-pentyne-2,3-diol on treatment with mercuric chloride proceeds through the step of formation of substituted β-chloromercurifurans, as we had also found in the case of some other α-glycols of the acetylenic series.

2. It was observed that the corresponding intermediate β-chloromercurifurans could not be isolated when acetone was used as the solvent in this reaction. In this case the substituted furans are obtained directly.

3. 2,3,5-Triphenyl-4-chloromercuri- and 2,3-dimethyl-5-phenyl-4-chloromercurifurans not described in the literature were synthesized.

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ALKYLATION OF AROMATIC COMPOUNDS BY DIENIC HYDROCARBONS

III. ALKENYLATION OF PHENOL BY PIPERYLENE IN PRESENCE OF ANHYDROUS PHOSPHORIC ACID

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The alkylation of phenols by dienic hydrocarbons has been studied more thoroughly than the alkylation of other aromatic compounds. Diolefins containing conjugated bonds were first used in the synthesis of compounds of the type of chroman [1], and they were later used for preparation of tocopherol (vitamin E) and of substances with similar action [2]. Condensation of piperylene with trimethylhydroquinone thus yielded 5,7,8-trimethyl-2-ethyl-6-hydroxychroman [3]. Only in isolated cases were intermediate products of reaction containing a double bond in the side chain observed [4]. In recent years the alkenylation of phenol has been effected with 1,3-butadiene [5], isoprene [6], and cyclopentadiene [7]. The reaction products are substituted p- and o-crotylphenols. One of us [8] showed that in dependence on the catalyst and the conditions the alkylation of phenolic ethers by piperylene can proceed stepwise, either stopping at the stage of formation of pentenyl derivatives or continuing to the stage of formation of diarylated products. The best alkenylation catalyst is anhydrous orthophosphoric acid.

In the present work we give details of the alkylation of phenol by piperylene in presence of orthophosphoric acid. In addition to the reaction courses already mentioned, we may expect in the case of phenol also alkenylation at the phenolic hydroxyl; polymerization and polycondensation can also be expected as secondary processes.

In the condensation of phenol with piperylene a study was made of the influence of dilution, temperature, and amount of catalyst on the yield and character of reaction products. Results are set forth in Table 1. Liquid and resinous products are formed. The yield of liquid product, calculated as pentenylphenol, is 50 to 78%; the content of resinous products is 12-13% of the total products.

Benzene was a convenient solvent for dilution of the reaction mixture since alkylation of the latter was not observed in presence of orthophosphoric acid. Under these conditions a considerable excess of phenol (more than two moles per mole of piperylene) is undesirable because the yield of liquid products remains the same (about 60%). Phosphoric acid was taken in the quantities which were optimum for alkylation of anisole [8] (1 : 0.25 molar ratio of piperylene to catalyst); with increasing proportion of catalyst the resin content increases (to 30%). With further dilution of the mixture with benzene (from 3.3 to 4.5 moles) or with gentle heating of the reaction mixture (35-40°), the yield of liquid products increases to 70-78%; rise of temperature to 70-75° promotes resinification.

Verification of the structure of the alkylation products was carried out separately for the sets of experiments run at 20-25° (series A), at 35-55° (series B), and at 70-75° (Expt. 13). It was found that the temperature influences not only the yield, but also the character of the alkylation products: with rising temperature of reaction the non-phenolic content increases (probably cyclic isomers) and the content of ortho-isomer increases. Thus at 20-25° the non-phenolics amount to 0.5% of the total liquid alkylation products, while at 70-75° they amount to 11.4% of the total.

The main component of the mixtures of pentenylphenols obtained under various conditions is 4-(p-hydroxyphenyl)-2-pentene (I). Its structure was confirmed by transformation by us [9] into the crystalline 2,3-dibromo-(p-methoxyphenyl)pentane, described in the literature, and into the p-(α-methylcrotyl)phenoxyacetic acid (VI), which has not been described. The latter was obtained from all fractions of pentenylphenols apart from the low-boiling fractions in series A and B (see Table 2). In the low-boiling fractions of these series was found

TABLE 1. Alkylation of Phenol by Piperylene in Presence of 100% Orthophosphoric Acid

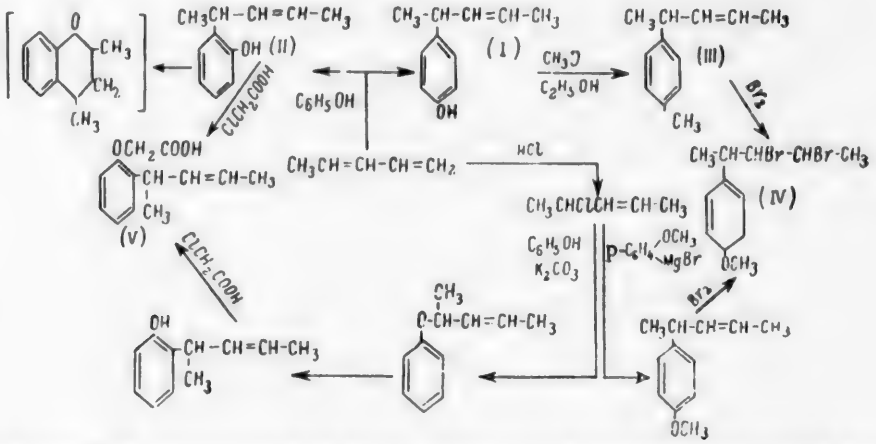
Expt. no.	Piperylene* per phenol/ orthophosphoric acid molar ratios	Amt. of benzene (moles)	Reaction temperature	Duration of heating (hr)	Duration of stirring (hr)	Yield of liquid products (%)	Amount of resinous residue (in %)**
1	1 : 2 : 0.25	3.3	20—25°	—	16	60.5	14.2
2	1 : 2 : 0.25	3.3	20—25	—	47	61.3	13.9
3	1 : 3 : 0.25	3.3	20—25	—	20	60.9	11.6
4	1 : 4 : 0.25	3.3	20—25	—	20	60.2	13.6
5	1 : 2 : 0.25	4.5	20—25	—	20	70.4	12.4
6	1 : 2 : 0.25	6.8	20—25	—	20	67.8	13.9
7	1 : 2 : 0.5	3.3	20—25	—	16	62.2	14.2
8	1 : 2 : 0.5	6.8	20—25	—	21	60.2	25.2
9	1 : 2 : 1	3.3	20—25	—	10.5	65.8	30.0
10 ***	1 : 2 : 0.25	3.3	35—40	8	13	78.4	19.7
11	1 : 2 : 0.25	3.3	50—55	7	12	64.6	21.7
12	1 : 3 : 0.25	1.1	45—50	9	10	58.1	21.6
13 ***	1 : 2 : 0.25	3.3	70—75	6	9.5	48.8	35.2

*Quantity of piperylene 17 g.

**Relative content in percentages of sum of reaction products, including residue from distillation.

***The temperature of the reaction mixture rose to 35° during addition of the piperylene.

4-(o-hydroxyphenyl)-2-pentene (II); from these fractions was obtained o-(α-methylcrotyl)phenoxyacetic acid (V), which has been described in the literature. The steps involved in the proof of structure of the pentenylphenols may be represented as follows:



We did not succeed in the realization of an alternative synthesis of 4-(p-hydroxyphenyl)-2-pentene (I) by demethylation of 4-(p-methoxyphenyl)-2-pentene (III) with the help of hydrogen iodide and hydrogen bromide in a medium of glacial acetic acid.

EXPERIMENTAL

The piperylene used in the experiments had b.p. 40.5-42.5°, $n^{20}D$ 1.4251, d^{20}_4 0.6835; the phenol had b.p. 93-94° (20 mm), m.p. 41.5-42.5°; the phosphoric acid had d 1.87.

Alkylation of phenol by piperylene was carried out in the apparatus described earlier [9] with addition in the course of an hour of 25 ml of piperylene dissolved in 25 ml of benzene to the mixture of phenol, catalyst, and benzene. During the piperylene addition the temperature was held at 20-25° by cooling; only in isolated experiments

TABLE 2. Derivatives of Pentenylphenols

Series*	Fraction No.	Pentenylphenols: boiling point (pressure in mm)	yield (%)	n_D^{20}	d_4^{20}	Pentenylphenoxyacetic acid: yield (%)	melting point	Yield of 2,3-dibromo-(p-methoxyphenyl) pentane (in %)
A	1	123—125° (9)	6.3	1.5307	0.9828	40	129—130° **	—
	2	125—127.5 (9)	11.3	1.5339	0.9908	50	79—81	—
	3	114—115 (5)	99.8	1.5350	0.9897	45	78.5—79.5 ***	93.2
	4	116—118 (5)	88.8	1.5350	0.9900	45	78—79	—
	5	111—114 (2)	1.5	1.5343	0.9886	—	—	—
B	1	126—128 (10)	6.0	1.5320	0.9848	38	127—129 **	—
	2	128—130 (10)	13.4	1.5339	0.9879	40	74—77.5	—
	3	119—120 (6)	50.7	1.5347	0.9890	52	78—79 ***	85.4
Expt. 13	1	118—120 (6)	13.6	1.5325	0.9851	46	79—81 ***	64.2

* Fractional distillation of liquid fractions in experiments carried out (A) at 20-25°, (B) at 35-55°, Expt. 13 at 70-75°; in series A fractional distillation gave 0.2% of phenol, in Expt. 13 the yield of phenol was 3.5%.

** No depression in a mixed melting point test with 4-(o-hydroxyphenyl)-2-pentenylphenoxyacetic acid.

*** A mixture with o-(α-methylcrotyl)phenoxyacetic acid melts at 76-93°.

was spontaneous heating of the mixture permitted. After the piperylene had been added, the mixture was stirred at room temperature (standing of the mixture without stirring did not influence the yield), after which it was heated or at once treated with water. Towards the end of the piperylene addition the reaction mixture usually turned yellow, and the color later changed to crimson. The reaction mixture was worked up in the usual manner. Excess phenol was taken off in vacuo in a Favorskii flask equipped with an air condenser. Products of alkylation were distilled in a flask fitted with a water condenser. The total boiling range of the liquid products was 7 to 50°; the main portion of alkylation product distilled within 3-4°. The resinous residue in the flask solidified on cooling. Conditions in individual experiments and results are set forth in Table 1.

With the aim of separating possible isomers, fractions were redistilled fractionally from a Favorskii flask in experiments performed at 20-25, 35-55, and 70-75°. Non-phenolic substances were isolated by treatment with 5% caustic alkali solution of all the fractions obtained in the fractional distillations. The non-phenolic portion was separated from the alkaline solution by extraction with ligroin; the phenolic portion (after acidification) was isolated by extraction with ether.

The following results were obtained in fractional distillation of the non-phenolic substances:

Series A. From 215.5 g of alkylation product taken for fractional distillation was isolated 1.1 g (0.5%) of non-phenolic substances in the form of a readily mobile liquid with a pleasant odor. B.p. 92-95° (4 mm), 98-108° (12 mm), $n^{20}D$ 1.5282-1.5300.

Series B. From 77 g of liquid product was isolated 1.57 g (2%) of non-phenolic substances. B.p. 80-95° (3 mm), $n^{20}D$ 1.5267-1.5295.

Experiment 13. From 18.2 g of liquid product taken for treatment with alkali was isolated 2 g (11.4%) of non-phenolic substances. B.p. 84-92° (3.5 mm), $n^{20}D$ 1.5272-1.5289.

Results of fractional distillation of pentenylphenols and derivatives are set forth in Table 2.

Pentenylphenol phenoxyacetic acids were prepared by the usual route [10]. Yields and melting points relate to products after recrystallization from ligroin. The following aryloxyacetic acids were isolated.

a) o-(α-Methylcrotyl)phenoxyacetic acid (V). M.p. 129-130° [11], M 222. $C_{13}H_{16}O_3$. A mixture with a specimen of o-(α-methylcrotyl)phenoxyacetic acid obtained from 4-(o-hydroxyphenyl)-2-pentene did not exhibit a depression of melting point. Compound (V) was isolated from the lower boiling pentenylphenol fractions in series A and B.

b) p-(α-Methylcrotyl)phenoxyacetic acid with m.p. 78.5-79.5° (lustrous, white plates), not described in the literature.

Found M 220.8, 221.6. $C_{13}H_{16}O_3$. Calculated M 220.3.

A mixture with o-(α-methylcrotyl)phenoxyacetic acid (V) melts at 76-93°. The acid was isolated from the main pentenylphenol (I) fractions (3 and 4 in series A and 3 in series B). A mixture of acids was obtained from the intermediate fractions in the same series as well as in Expt. 13.

Methylation of the main fractions of pentenylphenols. To a solution of sodium ethoxide prepared from 3.4 g of sodium and 100 ml of absolute alcohol were added 24.3 g of pentenylphenol and 23.6 g of methyl iodide. The mixture was heated on a water bath for 4 hr at 50-55° and for 2 hr at 80°. After the usual working-up (extraction with ligroin and washing of the phenol with 5% sodium hydroxide solution), the pentenylanisoles were fractionated from a Favorskii flask in vacuo. Yields and constants of the main fractions of pentenylanisole are given below.

Series A, 3rd fraction. Fractionation of the product of methylation gave 20.2 g (76.5%) of pentenylanisole with b.p. 86-87° (2 mm), $n^{20}D$ 1.5172, d^{20}_4 0.9515. Judging by its constants, the product is 4-(p-methoxyphenyl)-2-pentene (III).

Compound (III), as synthesized by the Grignard–Wurtz method [9], has b.p. 83-86° (3 mm), $n^{20}D$ 1.5190, d^{20}_4 0.9512; the product of alkylation of anisole by piperylene [8, 9] has b.p. 86.5-87° (1 mm), $n^{20}D$ 1.5170-1.5182, d^{20}_4 0.9501-1.5123.

Series B, 3rd fraction. There was obtained 77% of pentenylanisole with b.p. 102° (7 mm), $n^{20}D$ 1.5161, d^{20}_4 0.9437.

Experiment 13. There was obtained 64.7% of pentenylanisole with b.p. 105-106° (7 mm), $n^{20}D$ 1.5139, d^{20}_4 0.9428. The constants of pentenylanisoles isolated in experiments at higher temperatures are lower than those of (III).

Bromination of pentenylanisoles was performed by the procedure described earlier [9]. In all cases a dibromide with m.p. 72-73° (8, 9] was isolated. No depression of melting point in admixture with 2,3-dibromo-(p-methoxyphenyl)-pentane [9].

The high yields of dibromide (IV) (93.85 and 64%, see Table 2) indicate a predominating content in all the main fractions of 4-(p-hydroxyphenyl)-2-pentene.

The results also indicate that the 3rd and 4th fractions of pentenylphenol, isolated at room temperature, are purer 4-(p-hydroxyphenyl)-2-pentene. After combination of the 3rd and 4th fractions (series A), treatment with 10% alkali solutions, and refractionation, the 4-(p-hydroxyphenyl)-2-pentene (I) has the following constants:

B.p. 96.5-98° (4 mm), $n^{20}D$ 1.5370, d^{20}_4 0.9920, MR_D 51.07.

$C_{11}H_{14}OF_4$. Calculated 50.41.

Found %: C 81.02, 81.23; H 8.98, 8.82. $C_{11}H_{14}O$. Calculated %: C 81.44; H 8.70.

Synthesis of 4-(o-hydroxyphenyl)-2-pentene (II) [11, 12]. 4-Chloro-2-pentene was obtained by hydrochlorination of piperylene [9, 13].

α, γ-Dimethylallylphenyl ether [12] was obtained by heating of a mixture of 24.5 g of phenol, 36.5 g of 4-chloro-2-pentene, 39.75 g of anhydrous potassium carbonate, and 45 g of acetone on a water bath for 5 hr. Yield 12.6 g (27.6%).

B.p. 120-125° (30 mm), $n^{20}D$ 1.5090, d^{20}_4 0.9568. Literature data [12]: b.p. 96-98° (13 mm), $n^{20}D$ 1.5110, d^{20}_4 0.9510.

4-(o-Hydroxyphenyl)-2-pentene (II). Claisen rearrangement [11, 12] was effected by heating for an hour at 210° of 10.6 g of α, γ-dimethylallylphenyl ether. Yield 3.2 g (31%).

B.p. 140-150° (20 mm), $n^{20}D$ 1.5340, d^{20}_4 1.0070. Literature data [12]: b.p. 118-119° (12 mm), d^{15}_{15} 0.993. B.p. 87° (0.3 mm), $n^{20}D$ 1.5360.

o-(α-Methylcrotyl)phenoxyacetic acid (V) was prepared from 4-(o-hydroxyphenyl)-2-pentene with m.p. 129-130° (from ligroin). Literature data [11]: m.p. 128-130°.

SUMMARY

1. The alkylation of phenol by piperylene in presence of anhydrous orthophosphoric acid was studied. It was found possible to alkenylate a number of phenols with piperylene to give pentenylphenols in a yield of 78%. The reaction gives a mixture of para- and ortho-isomers of pentenylphenol, in which the former predominates, and substances of non-phenolic character (probably cyclic isomers). The temperature influences the yield and nature of the products formed.

2. Alkenylation proceeds with formation of 4-(p- and o-hydroxyphenyl)-2-pentenes—products of 1,4-addition in accordance with the electron density distribution in the piperylene molecule.

3. 4-(p-Hydroxyphenyl)-2-pentene was prepared and characterized for the first time.

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THE DIECKMANN REACTION

VIII. CYCLIZATION OF THE DIETHYL ESTER OF α-METHYL-α'-CARBETHOXYPIMELIC ACID

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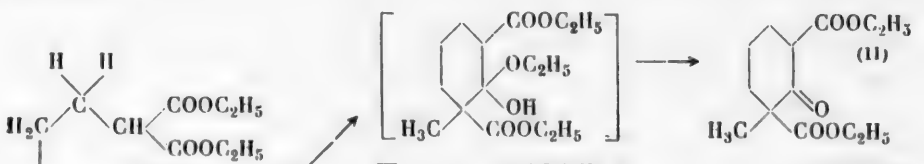
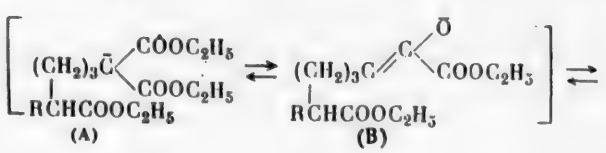
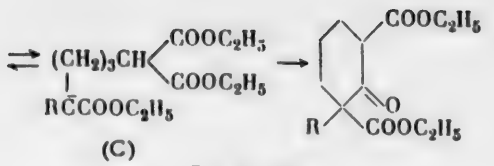
In continuation of our work on the Dieckmann reaction [1] we have investigated the cyclization of diethyl α-methyl-α'-carbethoxypimelate (I). We showed previously [2, 3] that cyclization of the diethyl esters of α-methyl- and α-carbethoxypimelic acids proceeds at the unsubstituted α-carbon atom and leads to 2-methyl-6-carbethoxy- and 2,6-dicarbethoxycyclohexanone, respectively. During preparation of the latter, as we later established, a very small quantity (about 2%) of 2-carbethoxycyclohexanone is also formed, i.e, cyclization also proceeds in this case to some extent at the substituted α-carbon atom.

It was interesting to establish the direction of cyclization of ester (I), which contains both a methyl and a carbethoxy group in the α,α'-positions. It was found that in alcoholic sodium ethoxide or potassium ethoxide solution ester (I) does not cyclize, whereas heating of the potassium derivative of ester (I) in vacuo at 140° leads to cyclization to give a mixture of 2-methyl-2,6-dicarbethoxycyclohexanone (II) and 2-methyl-6-carbethoxycyclohexanone (III) in 10 : 1 ratio. The ratio of (II) to (III) alters to 1.5 : 1 when an excess of potassium ethoxide is used [1.5 moles per mole of ester (I)].



Consequently, in spite of the blocking effect of the methyl group (the + J effect which increases the electron density at the α-carbon and hinders dissociation of the proton and formation of the organic ion needed for cyclization), cyclization of ester (I) proceeds preferentially at the α-carbon linked to this group. These results, like those of our earlier study of cyclization of diethyl α-carbethoxypimelate [3], point to factors hindering reaction at the α-carbon linked to the carbethoxy group. It may be surmised that in both cases the A⇌B equilibrium is heavily shifted to the right. The resulting enolate (B) is incapable of cyclization, and on heating it rearranges to anion (C), which then cyclizes to a derivative of 2,6-dicarbethoxycyclohexanone.



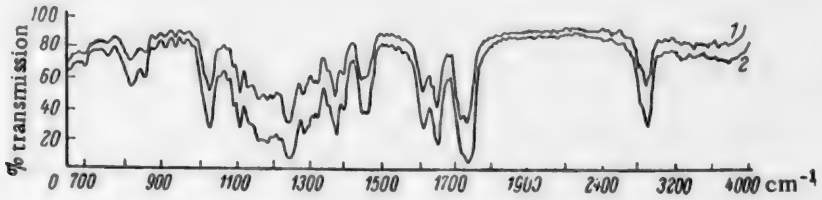


(C)

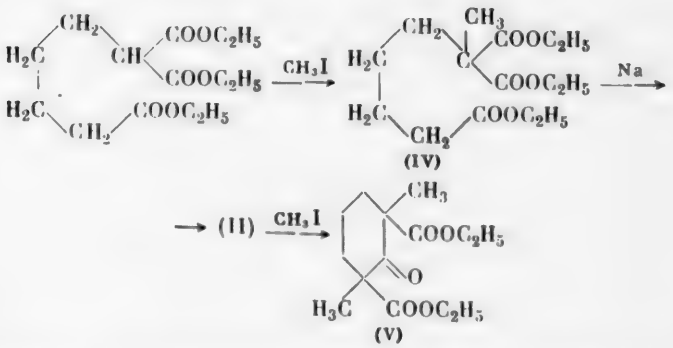
R = H, CH_3.

The facility of cyclization of diethyl β-methyl-α,α'-dicarbethoxypimelate [4] is evidently attributable to cyclization of an anion of type (A) (R = $COOC_2H_5$) in the first instance in small quantity, and to gradual shift of the A ⇌ B equilibrium to the left. Moreover the formation from ester (I) of a derivative of 2,6-dicarbethoxycyclohexanone is evidently sterically favored.

The structure of our 2-methyl-2,6-dicarbethoxycyclohexanone (II) is confirmed by the complete identity between its infrared spectrum and that of the authentic compound (see figure), synthesized by methylation of the diethyl ester of α-carbethoxypimelic acid and subsequent cyclization of the resulting diethyl α-methyl-α-carbethoxypimelate (IV) by the Dieckmann reaction. Methylation of (II) gave 2,6-dimethyl-2,6-dicarbethoxycyclohexanone (V).



Infrared spectra. 1) 2-Methyl-2,6-dicarbethoxycyclohexanone prepared by cyclization of ester (IV); 2) 2-methyl-2,6-dicarbethoxycyclohexanone prepared by cyclization of ester (I).



(IV)

(V)

The structure of 2-methyl-6-carbethoxycyclohexanone (III) was confirmed by the preparation of its phenylhydrazone; the latter was identical with the product of alternative synthesis.

We synthesized the initial ester (I) by two routes: a) From 1-chloro-3-bromopropane via diethyl γ-chloropropylmethylmalonate and ethyl δ-bromo-α-methylvalerate, condensation with sodium malonic ester, hydrolysis, and decarboxylation; b) by reaction of diethyl α-methylpimelate with diethyl oxalate followed by decarboxylation of the resulting diethyl α-methyl-α'-ethoxypimelate.

EXPERIMENTAL

Diethyl γ-chloropropylmethylmalonate. To a solution of sodium ethoxide (11.5 g of sodium in 150 ml of absolute alcohol) was added 87 g of diethyl malonate, and the mixture was boiled for 40 min. After cooling to 60°, addition was gradually made (20 min) with stirring of 78.75 g of 1-chloro-3-bromopropane, and the boiling mass was stirred for 5 hr (towards the end the mass had a pH of about 7). The mass was made acid to litmus by addition of 0.3 ml of glacial acetic acid, and 130 ml of alcohol was distilled off with stirring. The residue was cooled and

poured into a mixture of 375 ml of dilute (1 : 5) hydrochloric acid and a small quantity of ice at 5-6°. After ether extraction, the ethereal solution was washed with 5% sodium carbonate solution and with water, and then dried with sodium sulfate. The ether was driven off and the residue distilled to give 45.3 g (36.1%) of ester.

B.p. 143.5-145° (12 mm), d^{25}_4 1.0882, $n^{25}D$ 1.4430, MR_D 61.03; calc. 61.17.

Found %: Cl 14.01, 13.98. $C_{11}H_{19}O_4Cl$. Calculated %: Cl 14.14.

Ethyl δ-bromo-α-methylvalerate. A mixture of 57.7 g of diethyl γ-chloropropylmethylmalonate was stirred for an hour with 230 ml of 47.5% hydrobromic acid under reflux. A mixture of ethyl bromide and hydrobromic acid was then gradually taken off through a column with a distillation attachment. After 6 hr the temperature had reached 125-127°. At this temperature distillation was carried out for another 4 hr (the total volume of distillate was 224 ml). The residue was treated with 65 ml of water and twice extracted with ether; the extract was washed with water and dried with sodium sulfate. After distillation of the ether, the residue was dehydrated by azeotropic distillation with benzene. The residual benzene was removed by heating for 10-15 min to 180° at about 180 mm. The crude δ-bromo-α-methylvaleric acid (34.3 g) was boiled for 6 hr with 280 ml of absolute alcohol and 4 ml of conc. H_2SO_4. The alcohol was distilled and the residue poured into 400 ml of water; an oil separated; the aqueous layer was extracted with ether, and the combined oil and extract were washed with 10% sodium carbonate solution and with water, and then dried with sodium sulfate. After removal of the ether, the residue was distilled to give 29.6 g of ester.

B.p. 92.5-96.5° (7.5 mm), d^{25}_4 1.2294, $n^{25}D$ 1.4520, MR_D 48.68; calc. 48.56.

Found %: Br 35.65, 35.44. $C_8H_{15}O_2Br$. Calculated %: Br 35.82.

Redistillation of the foredistillate and of the higher boiling fraction gave another 3.5 g. Total yield 64.5% (calculated on diethyl γ-chloropropylmethylmalonate).*

Diethyl α-methyl-α'-carbethoxypimelate (I). a) To a solution of sodium malonic ester (from 62.5 g of malonic ester, 3 g of sodium, and 60 ml of absolute alcohol) was added 0.5 g of sodium iodide; 29 g of ethyl δ-bromo-α-methylvalerate was then run in, and the mixture gradually brought to the boil with stirring. After boiling for 5 hr, the mass was acidified with a few drops of glacial acetic acid (weak reaction to litmus), and 20 ml of alcohol was distilled off. The residue was cooled, run into 200 ml of water (8-12°), and extracted with ether. The extract was washed with water, with 20% sodium thiosulfate solution (50 ml), and again with water. After drying with sodium sulfate, the ether was removed and the residue distilled to give 32.8 g (83.5%).

B.p. 102-103.5° (0.04 mm), d^{25}_4 1.0328, $n^{25}D$ 1.4355, MR_D 76.38; calc. 76.43.

Found %: C 59.82, 59.73; H 8.53, 8.56. $C_{15}H_{28}O_6$. Calculated %: C 59.60; H 8.61.

b) To a suspension of 2.35 g of potassium powder in 65 ml of absolute ether was added a mixture of 2.76 g of absolute alcohol and 7 ml of absolute ether dropwise at 3-14°. The mass was stirred at 20-22° until the potassium had dissolved (10-15 min), and cooled to 2°. In the course of 5-7 min 8.76 g of diethyl oxalate was run in at 2-7°. The mass was again cooled to 2° and in the course of 15 min 13.8 g of diethyl α-methyl pimelate was run in. The mixture was stirred at room temperature for 20 min and left overnight. To the viscous, yellow mass was added ice in small portions with cooling from 0 to −20°, then 30-40 ml of water was added at −10 to −15°, and the precipitate in the aqueous layer was dissolved. The ether layer was separated; the aqueous layer was extracted with 30 ml of ether and acidified at 3-5° with 20% sulfuric acid; the oil was extracted with ether and the extract washed with water, with 5% sodium bicarbonate solution, and again with water. After drying with sodium sulfate, the extract was divided into two portions for further treatment. The ether was driven off; to the residue were added 0.3 g of glass powder and a grain of iron powder. The residue was then heated in vacuo (9-10 mm). Violent evolution of gas started at 170° (bath temperature). Pyrolysis was continued for about 40 min (the bath temperature was raised to 180°). The reaction product was distilled and two fractions collected: 1st, b.p. 162-165° (7.5 mm), $n^{25}D$ 1.4350, 0.23 g; 2nd, b.p. 165-167° (7-7.5 mm), d^{25}_4 1.0318, $n^{25}D$ 1.4355, 3.74 g (41.2%). Total yield 3.97 g (43.8% calculated on the diethyl-α-methylpimelate).

Trihydrazide of α-methyl-α'-carboxypimelic acid. A mixture of 0.6 g of ester (I), 1.2 ml of hydrazine hydrate, and 1.3 ml of absolute alcohol was boiled for 2 hr, and 0.46 g (80%) of a colorless, crystalline substance was

* Literature data [5]: b.p. 108-110° (2 mm); probably a misprint—should be 12 mm.

obtained with m.p. 175.5-176.5° (decomp., from 70% alcohol); no depression of melting point in admixture with a specimen prepared from substance (I) by method "a".

Found %: C 41.32, 41.50; H 7.62, 7.75; N 32.18, 32.20. $C_9H_{20}O_3N_6$. Calculated %: C 41.52; H 7.74; N 32.29.

Cyclization of diethyl α-methyl-α'-carbethoxypimelate (I). To a solution of potassium ethoxide (from 0.39 g of potassium and 6.2 ml of anhydrous alcohol) was added 3.02 g of ester (I), and the mixture was gradually heated while the alcohol distilled off. At 100° the apparatus was connected to a vacuum (150 mm), and heating continued for about an hour with distillation of the alcohol and gradual lowering of pressure to 115 mm and raising of temperature to 140°. Heating at 140° was carried out for 40 min with lowering of pressure to 50 mm, after which heating was continued under the same conditions for another 4.5 hr. The red mass solidified on cooling and was boiled with 10 ml of ether, cooled to −12°, treated with a small quantity of ice, and (at −10 to −12°) acidified with dilute (1 : 1) hydrochloric acid until acid to Congo. The solid mass was stirred and gradually changed into an oil which was dissolved in ether. The ethereal layer was separated, the aqueous layer extracted with ether, and the combined extracts washed with 3 ml of 5% sodium carbonate solution and with water, and dried with sodium sulfate. The ether was driven off, and the residue distilled to give two fractions: a) 0.08 g (4%) of 2-methyl-6-carbethoxycyclohexanone (III) with b.p. 45.5-50° (0.1 mm), $n^{25}D$ 1.4695; we previously prepared this substance [2] with b.p. 84.5-86° (2.5 mm), $n^{20}D$ 1.4720; the phenylhydrazone prepared by the method of [6] has m.p. 135-136° (from 70% alcohol), and does not give a depression in admixture with an authentic specimen (m.p. 136-137° [1]); b) 1.14 g (44.5%) of 2-methyl-2,6-dicarbethoxycyclohexanone (II) with b.p. 84-85° (0.04 mm), $n^{25}D$ 1.4650; we previously obtained this substance [3] with b.p. 112-114° (1 mm), $n^{20}D$ 1.4645-1.4655. Compounds (II) and (III) give a deep violet color with aqueous ferric chloride solution.

When cyclization was performed in presence of the 1.5-fold quantity of potassium ethoxide, 3.02 g of ester (I) gave 0.33 g (17.9%) of (III) and 0.69 g (26.9%) of (II).

Diethyl α-methyl-α-carbethoxypimelate (IV). At 20-22° a mixture of 50 ml of methyl iodide and 50 ml of absolute alcohol was added to a mixture of 179.7 g of diethyl α-carbethoxypimelate and a solution of sodium ethoxide (from 15 ml of sodium and 500 ml of absolute alcohol). After it had been stirred for 30 min, the mass was boiled for 2 hr and again stirred at about 20° until neutral to Brilliant Yellow paper (6 hr). Part of the alcohol was distilled in a low vacuum and the residue poured into a liter of water (4-7°), acidified with dilute hydrochloric acid until weakly acid to Congo, and extracted with ether. The extract was washed with 0.1 N sodium thiosulfate solution (4 × 50 ml) and then with water, and dried with sodium sulfate. After removal of the ether, the residue was distilled to give 172 g (91.2%).

B.p. 146.5-153° (3 mm), d^{20}_4 1.0401, $n^{20}D$ 1.4375, MR_D 76.19; calc. 76.43.

Found %: C 59.47, 59.43; H 8.61, 8.62. $C_{15}H_{26}O_6$. Calculated %: C 59.60; H 8.61.

Diethyl α-methyl-α-carbethoxypimelate (IV) can also be obtained from the alcoholic solution after condensation of 24.5 g of ethyl δ-chlorovalerate with malonic ester if, as previously described [7], this is treated without isolation of the resulting α-carbethoxypimelic ester with a solution of sodium ethoxide (from 5.75 g of sodium in 100 ml of absolute alcohol) at 20-23° for about an hour, and then methylated with 20 ml of methyl iodide in the above manner. Yield of ester (IV) 33.1 g (73.7%); b.p. 130-137° (1.5-2 mm).

2-Methyl-2,6-dicarbethoxycyclohexanone (II). To a suspension of 1.6 g of sodium powder in 50 ml of dry xylene were added in one portion 15.1 g of ester (IV) and 0.1 ml of absolute alcohol. The mixture was carefully heated and stirred until a violent reaction commenced (about 126°). Steady boiling was maintained by interrupting the heating and periodically cooling the mass. After dissolution of the sodium (about 15 min), boiling was continued for 5 hr. The mass was then cooled, poured onto 100 g of ice, acidified at a temperature not higher than 0° with dilute (1 : 1) hydrochloric acid (test with Congo), and extracted with 50 ml of benzene. The extract was washed with 5% sodium carbonate solution and with water, dried with sodium sulfate, and distilled to give 5.7 g (44.6%) of ester (II). With aqueous ferric chloride solution the product gave a deep violet coloration.

B.p. 107.5° (~ 1 mm), 94.5-95.5° (0.09 mm), d^{20}_4 1.1021, $n^{20}D$ 1.4705, $n^{25}D$ 1.4695, MR 64.82; calc. for enol 64.40, for ketone 63.85.

Found %: C 60.76, 60.74; H 7.96, 7.86. $C_{13}H_{20}O_5$. Calculated %: C 60.94; H 7.81.

2,6-Dimethyl-2,6-dicarbethoxycyclohexanone (V). To a mixture (cooled to −12°) of 12.8 g of ester (II), 27 ml of anhydrous methanol, and 5 ml of methyl iodide was added in the course of 5 min a solution of sodium methoxide (from 1.3 g of sodium and 25 ml of anhydrous methanol). The mass was stirred at 0 to −1° for an hour and boiled until neutral to Brilliant Yellowpaper (75 min). The methanol was distilled off and the cooled residue poured into 200 ml of cold water and extracted with ether. The extract was washed with 25 ml of 15% potassium hydroxide solution, with 0.1 N sodium thiosulfate solution (3 × 50 ml), with cooled (about 0°) 15% potassium hydroxide solution (until the reaction with ferric chloride solution was negative (3 × 25 ml), and with water. After removal of the ether, the residue was distilled to give 9.7 g (71.8%) of substance (V); no reaction with aqueous ferric chloride solution.

B.p. 113.5-114.5° (2 mm), d^{20}_4 1.0926, $n^{20}D$ 1.4605, MR_D 67.81; calc. 67.97.

Found %: C 62.03, 62.26; H 8.12, 8.26. $C_{14}H_{22}O_5$. Calculated %: C 62.22; H 8.15.

2,6-Dimethyl-2,6-dicarbethoxycyclohexanone (V) had the following constants when previously prepared [3]:

B.p. 123.5-126.5° (3 mm), 117-117.5° (2 mm), d^{20}_4 1.0860-1.0940, $n^{20}D$ 1.4615.

The infrared spectra were plotted with a Hilger N-800 two-beam spectrophotometer with a NaCl prism by L. B. Senyavina, to whom the authors extend their profound gratitude.

SUMMARY

1. It was shown that cyclization of diethyl α-methyl-α'-carbethoxypimelate proceeds with formation of a mixture of 2-methyl-6-carbethoxy- and 2-methyl-2,6-dicarbethoxycyclohexanone in which the latter predominates considerably.

2. The structure of 2-methyl-2,6-dicarbethoxycyclohexanone was confirmed by the identity of its infrared spectrum with the spectrum of an authentic specimen prepared by alternative synthesis from diethyl α-methyl-α-carbethoxypimelate.

3. 2-Methyl-6-carbethoxycyclohexanone was identified by comparison of its phenylhydrazone with an authentic specimen.

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SYNTHESIS OF DERIVATIVES OF 2-ALKYL-5-METHOXYGRAMINE

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In one of our investigations [1],* 1-benzyl-2-methyl-5-methoxygramine was obtained as an intermediate in the synthesis of preparation BAS. According to K. S. Shadurskii this intermediate is highly active as an antimetabolite of serotonin. This fact and the very great interest of foreign workers [2, 3] in other indole derivatives prepared by us [1, 4-6] prompted us to report in the present paper on our work on synthesis of a series of derivatives of 5-methoxygramine.

Reaction of p-benzoquinone with derivatives of β-aminocrotonic ester gave: 1-butyl-2-methyl-3-carbethoxy-5-hydroxyindole (I), 1-benzyl-2-propyl-3-carbethoxy-5-hydroxyindole (II), and 1-benzyl-2-heptadecyl-3-carbethoxy-5-hydroxyindole (III). Methylation of hydroxyindoles (I-III) by dimethyl sulfate gave: 1-butyl-2-methyl-3-carbethoxy-5-methoxyindole (IV), 1-benzyl-2-propyl-3-carbethoxy-5-methoxyindole (V), and 1-benzyl-2-heptadecyl-3-carbethoxy-5-methoxyindole (VI). Decarbethoxylation of methoxyindoles (IV-VI) and of 1-ethyl-2-methyl-3-carbethoxy-5-methoxyindole gave the following (previously synthesized [5]) compounds: 1-ethyl-2-methyl-5-methoxyindole (VII), 1-butyl-2-methyl-5-methoxyindole (VIII), 1-benzyl-2-propyl-5-methoxyindole (IX), and 1-benzyl-2-heptadecyl-5-methoxyindole (X). Reaction of these derivatives of 5-methoxyindole (VII-X), and also of our previously prepared [7, 8] 2-methyl-5-methoxyindole and 1,2-dimethyl-5-methoxyindole, with formaldehyde and secondary amines gave: 2-methyl-3-dimethylaminomethyl-5-methoxyindole (XI), 2-methyl-3-piperidinomethyl-5-methoxyindole (XII), 1,2-dimethyl-3-dimethylaminomethyl-5-methoxyindole (XIII), 1-ethyl-2-methyl-3-dimethylaminomethyl-5-methoxyindole (XIV), 1-butyl-2-methyl-3-dimethylaminomethyl-5-methoxyindole (XV), 1-benzyl-2-methyl-3-diethylaminoethyl-5-methoxyindole (XVI), 1-benzyl-2-propyl-3-dimethylaminomethyl-5-methoxyindole (XVII), and 1-benzyl-2-heptadecyl-3-dimethylaminomethyl-5-methoxyindole (XVIII).

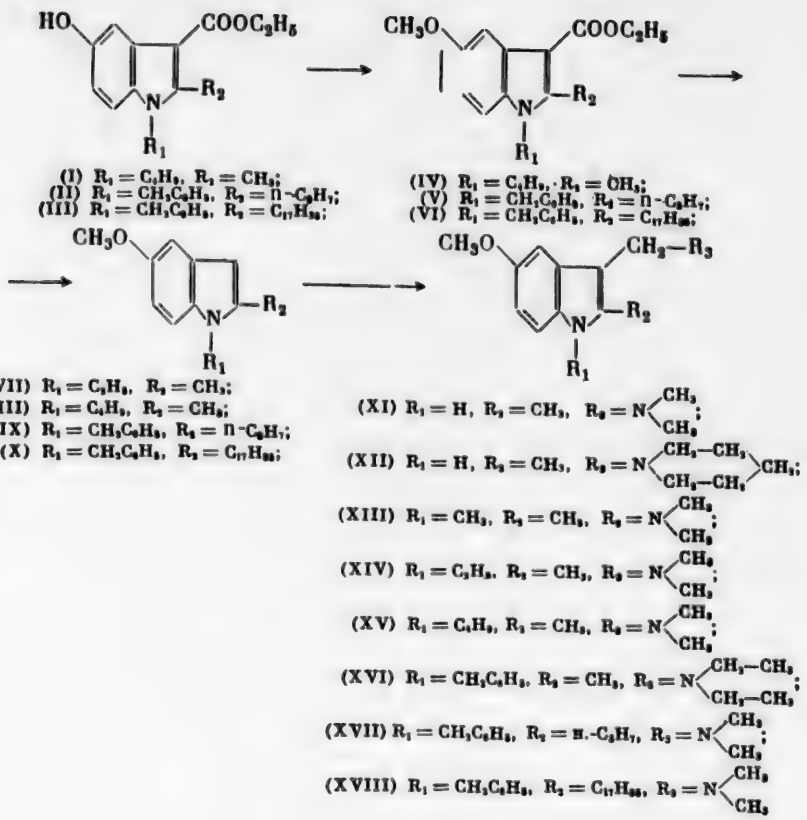
Results of pharmacological tests with the prepared derivatives of gramine (XI-XVIII) will be published separately.

EXPERIMENTAL

1-Butyl-2-methyl-3-carbethoxy-5-hydroxyindole (I). A mixture of 40.6 g of butylamine and 72.3 g of ethylacetoacetate was refluxed in a flask for 3 hr on a water bath. The aqueous layer was separated. To the resulting N-butyl-β-aminocrotonic ester was added 300 ml of dichloroethane, and the solution dried with magnesium sulfate. To the solution of N-butyl-β-aminocrotonic ester in dichloroethane were then added 220 ml of dichloroethane and 54 g of p-benzoquinone. The reaction mixture was boiled in a distillation flask for 45-60 min and 350 ml of solvent was taken off. After cooling, the deposited crystals of hydroxyindole (I) were filtered, washed with ether, and recrystallized from dioxane. Yield 41 g (30%), m.p. 147.5-148°.

Found%: C 69.63, 69.92; H 7.60, 7.90. $C_{16}H_{21}O_3N$. Calculated%: C 69.79; H 7.69.

* An error occurred in our paper [1] in the description of the synthesis of 1-benzyl-2-methyl-5-methoxyindolyl-3-acetonitrile. Instead of the stated quantity of 7.2 g of sodium cyanide, the quantity should be 12.3 g per 27 g of 1-benzyl-2-methyl-3-dimethylaminomethyl-5-methoxyindole methoiodide. Reduction of the nitrile by lithium aluminum hydride in ether under the usual conditions gave 1-benzyl-2-methyl-5-methoxytryptamine (preparation BAS) in 42% yield.


(I) R1 = C2H5, R2 = CH3;
(II) R1 = CH2C6H5, R2 = n-C3H7;
(III) R1 = CH2C6H5, R2 = C17H35;
(IV) R1 = C2H5, R2 = CH3;
(V) R1 = CH2C6H5, R2 = n-C3H7;
(VI) R1 = CH2C6H5, R2 = C17H35;
(VII) R1 = C2H5, R2 = CH3;
(VIII) R1 = C4H9, R2 = CH3;
(IX) R1 = CH2C6H5, R2 = n-C3H7;
(X) R1 = CH2C6H5, R2 = C17H35;
(XI) R1 = H, R2 = CH3, R3 = N(CH3)2;
(XII) R1 = H, R2 = CH3, R3 = N(CH2-CH2)2CH2;
(XIII) R1 = CH3, R2 = CH3, R3 = N(CH3)2;
(XIV) R1 = C2H5, R2 = CH3, R3 = N(CH3)2;
(XV) R1 = C4H9, R2 = CH3, R3 = N(CH3)2;
(XVI) R1 = CH2C6H5, R2 = CH3, R3 = N(CH2-CH2)2;
(XVII) R1 = CH2C6H5, R2 = n-C3H7, R3 = N(CH3)2;
(XVIII) R1 = CH2C6H5, R2 = C17H35, R3 = N(CH3)2

1-Benzyl-2-propyl-3-carbethoxy-5-hydroxyindole (II). Reaction conditions were as in the preceding experiment. The imine of butyroacetic ester was prepared from 10 g of butyroacetic ester and 6.7 g of benzylamine. The imine was not isolated. A solution of the imine in 100 ml of dichloroethane was used for preparation of hydroxyindole (II). Reaction was performed with 6.8 g of p-benzoquinone. Yield of purified hydroxyindole (II) 4.5 g (20%), m.p. 143-144° (from toluene).

Found %: C 74.92, 74.99; H 6.82, 6.90. $C_{21}H_{23}O_3N$. Calculated %: C 74.75; H 6.87.

1-Benzyl-2-heptadecyl-3-carbethoxy-5-hydroxyindole (III). Reaction was performed under the conditions of preparation of compound (I). The imine of stearylacetic ester was prepared from 92 g of stearylacetic ester and 28 g of benzylamine. The imine was not isolated. Hydroxyindole (III) was obtained by interaction of the imine with 28.1 g of p-benzoquinone in 450 ml of dichloroethane. In the course of 45 min 300 ml of solvent was taken off in the form of an azeotropic mixture with water. The residue was diluted with three volumes of ligroin , and the resulting solution cooled for 2 hr at −30°. The crystals were dried. Yield of hydroxyindole (III) 35 g (25.5%), m.p. 90-90.5° (from ligroin).

Found %: C 78.83, 78.65; H 9.53, 9.31. $C_{36}H_{51}O_3N$. Calculated %: C 78.75; H 9.63.

1-Butyl-2-methyl-3-carbethoxy-5-methoxyindole (IV). To a solution of 11.2 g of hydroxyindole (I) in 34 ml of dioxane were quickly added 40 ml of 2 N sodium hydroxide solution and 10 ml of dimethyl sulfate. The reaction mixture was shaken for 45 min at room temperature and diluted with three volumes of water. An oily layer formed and was separated. The aqueous layer was extracted with ether, the oily layer was added to the ethereal extract

and the whole dried over calcium chloride. After removal of the ether, the methoxyindole (IV) was distilled in vacuo. B.p. 213-214° at 3.5 mm; yield 10 g (85%).

Found %: C 70.13, 70.22; H 8.20, 8.32. $C_{17}H_{23}O_3N$. Calculated %: C 70.56; H 8.01.

Picrate, m.p. 117-117.5°.

Found %: N 10.87, 10.68. $C_{17}H_{23}O_3N \cdot C_6H_3O_7N_3$. Calculated %: N 10.81.

1-Benzyl-2-propyl-3-carbethoxy-5-methoxyindole (V). The reaction was carried out under the conditions of the preceding experiment, starting from 4 g of hydroxyindole (II), 20 ml of 2 N sodium hydroxide, 4 ml of dimethyl sulfate, and 8 ml of dioxane. Yield of methoxyindole (V) 3 g (75%); m.p. 63-65° (from alcohol).

Found %: C 75.50; H 7.14. $C_{22}H_{25}O_3N$. Calculated %: C 75.18; H 7.17.

1-Benzyl-2-heptadecyl-3-carbethoxy-5-methoxyindole (VI). The reaction was carried out under the conditions of preparation of (IV), starting from 32 g of hydroxyindole (III), 120 ml of 2 N sodium hydroxide, 24 ml of dimethyl sulfate, and 84 ml of dioxane. After dilution of the reaction solution with water, the emulsion was cooled for 2 hr at −3°. The resulting crystals were filtered, dried, and reprecipitated from ligroin with methanol. The crystals were filtered and recrystallized from a mixture of methanol and ligroin. Yield of methoxyindole (VI) 14 g; m.p. 61-62°.

Found %: C 78.72, 78.93; H 9.68, 9.83. $C_{36}H_{53}O_3N$. Calculated %: C 78.93; H 9.76.

1-Ethyl-2-methyl-5-methoxyindole (VII). To a boiling solution of 10 g of 1-ethyl-2-methyl-3-carbethoxy-5-methoxyindole [5] in 25 ml of acetic acid was added 10 ml of concentrated sulfuric acid in several portions. The resulting solution was refluxed for 20 min. It was then neutralized (ice cooling) with 2 N sodium hydroxide, and indole (VII) was distilled with steam. The distillate was allowed to cool in a refrigerator at 0°. The crystals were filtered and dried in a vacuum-desiccator at 0°. Yield 2.9 g (40%); m.p. 20-21°.

Found %: C 75.71, 76.03; H 8.13, 8.06. $C_{12}H_{15}ON$. Calculated %: C 76.15; H 7.99.

Picrate, m.p. 104-104.5°.

Found %: N 12.98, 13.13. $C_{12}H_{15}ON \cdot C_6H_3O_7N_3$. Calculated %: N 13.39.

1-Butyl-2-methyl-5-methoxyindole (VIII). To a solution of 10 g of (IV) in 25 ml of acetic acid was added (in several portions) a solution of 12 ml of concentrated sulfuric acid in 30 ml of acetic acid. The reaction solution was boiled for 18-20 min, cooled, and poured into a mixture of water and ice. The resulting oily layer was diluted with ether and dried with calcium chloride. After removal of the ether, the indole (VIII) was distilled in vacuo. B.p. 156-157° at 3.5 mm; yield 3.5 g (46%).

Found %: C 77.30, 77.11; H 9.23, 9.16. $C_{14}H_{19}ON$. Calculated %: C 77.38; H 8.81.

Picrate, m.p. 90°.

Found %: N 12.22, 12.25. $C_{14}H_{19}ON \cdot C_6H_3O_7H_3$. Calculated %: N 12.55.

1-Benzyl-2-propyl-5-methoxyindole (IX). Synthesis and separation of the compound were performed under the conditions of the preceding experiment. The original indole (V) was dissolved in 3 ml of acetic acid. A solution of 1.2 ml of concentrated sulfuric acid and 3 ml of acetic acid was prepared for the decarbethoxylation. Yield 0.6 g (45%); m.p. 65-66° (from alcohol).

Found %: C 81.47, 81.66; H 7.88, 7.97. $C_{19}H_{21}ON$. Calculated %: C 81.68; H 7.58.

1-Benzyl-2-heptadecyl-5-methoxyindole (X). Reaction components were 14 g of indole (VI), 9 ml of concentrated sulfuric acid, and 45 ml of acetic acid. Synthesis and isolation of the compound were performed under the conditions of preparation of compound (VIII). Yield 8.5 g (70%); m.p. 64-65° (from methanol).

Found %: C 83.09, 83.16; H 10.35, 10.16. $C_{33}H_{49}ON$. Calculated %: C 83.31; H 10.38.

2-Methyl-3-dimethylaminomethyl-5-methoxyindole (XI). To a solution of 3 g of 2-methyl-5-methoxyindole [8] in 6 ml of dioxane were added (with cooling) a previously cooled mixture of 2 g of dimethylamine hydrochloride (in the form of a 25% aqueous solution) and 0.9 ml of formalin. The reaction mixture was shaken for 4 hr at room

Synthesis of Derivatives of 2-Alkyl-5-methoxygramine

Taken for the expt.					Duration of reaction	Compound obtained	Yield (%)	Melting point	Empirical formula	Found (%)		Calculated (%)	
starting substances	indole (g)	formalin (ml)	amine (g)	dioxane (ml)						C	H	C	H
2-Methyl-5-methoxyindole, dimethylamine hydrochloride	3	0.9	2	6	4 hr	(XI), base*	57	161-162	$C_{13}H_{18}ON_2$	71.17 8.63	8.47 71.32	71.52	8.31
2-Methyl-5-methoxyindole, piperidine	0.5	0.5	0.2	1	4 hr	(XII), base**	80	134-136	$C_{16}H_{22}ON_2$	73.96	8.53	74.38	8.58
1,2-Dimethyl-5-methoxyindole, dimethylamine hydrochloride	3	1.3	2.8	13	2.5 hr	(XIII), base***	50	113	$C_{14}H_{20}ON_2$	72.34 72.31	8.52 8.59	72.38	8.68
1-Ethyl-2-methyl-5-methoxyindole (VII), dimethylamine hydrochloride	2.5	0.9	2.1	3	4 hr	(XIV), hydrochloride	50	157-157.5	$C_{15}H_{22}ON_2 \cdot HCl$	63.74 63.97	8.12 8.35	63.64	8.13
1-Butyl-2-methyl-5-methoxyindole (VIII), dimethylamine hydrochloride	3.2 /	1.	2.4	4	1 day	(XV), hydrochloride	77	160-161	$C_{17}H_{26}ON_2 \cdot HCl$	65.21 65.37	8.90 8.89	65.61	8.68
1-Benzyl-2-methyl-5-methoxyindole (VIII), diethylamine hydrochloride	2	0.56	1.76	Up to complete solution of the reaction mixture	6 days	(XVI), base****	70	163	$C_{22}H_{22}ON_2$	79.10	8.73	78.53	8.39
1-Benzyl-2-propyl-5-methoxyindole (IX), dimethylamine hydrochloride	0.4	0.1	0.2		4 hr	(XVII), hydrochloride	80	156-157	$C_{22}H_{28}ON_2 \cdot HCl$	70.92 70.74	7.74 7.92	70.77	7.77
1-Benzyl-2-heptadecyl-5-methoxyindole (X), dimethylamine hydrochloride.	4.7	0.8	1.6	the same	6 days	(XVIII), hydrochloride	80	128-129	$C_{36}H_{56}ON_2 \cdot HCl$	75.64 76.05	10.18 10.28	75.88	10.10

*Picrate, b.p. 136-137°. Found %: N 15.75, 15.55. $C_{13}H_{18}ON_2 \cdot C_6H_3O_7N_3$. Calculated %: N 15.65.

**Picrate, b.p. 156-157°. Found %: N 14.15, 14.07. $C_{16}H_{22}ON_2 \cdot C_6H_3O_7N_3$. Calculated %: N 14.37.

***Picrate, b.p. 140-141°. Found %: N 14.98, 15.04. $C_{14}H_{20}ON_2 \cdot C_6H_3O_7N_3$. Calculated %: N 15.18.

****Picrate, b.p. 113-114°. Found %: N 12.18, 12.28. $C_{22}H_{28}ON_2 \cdot C_6H_3O_7N_3$. Calculated %: N 12.38.

temperature and then poured into water. The resulting resin and unreacted original indole were separated. Mannich base (XI) was isolated from the aqueous solution after it had been made alkaline with 10% sodium hydroxide solution. The base was purified via the hydrochloride (see table).

The other derivatives of gramine (XII-XVIII) were similarly synthesized (see table).

SUMMARY

With the objective of carrying out pharmacological tests, a number of substituted gramines were synthesized on the basis of derivatives of 5-hydroxyindole.

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CONDENSED HETEROCYCLES

DERIVATIVES OF 1-PHENYL-PYRAZOLINO-[2,3-a]-PYRIMIDINE

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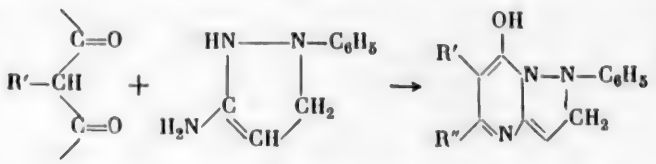
Condensed heterobicyclic pyrimidine systems play an extremely important part in various biochemical processes, particularly in the transmission of hereditary characteristics [1, 2]. On the other hand many carbazi condensed heterocycles are very effective inhibitors of the chemical ripening of photographic emulsions and therefore find application as stabilizers of cinema film materials. Particularly extensive use is made of 5-methyl-7-hydroxy-1,3,4-triazolo-[2,3-a]-pyrimidine (5-methyl-7-hydroxy-1,3,4-triazaindolizin) [3, 4]. Carbazicondensed pyrimidine systems are synthesized by condensation of β-dicarbonyl compounds with nitrogenous aminoheterocycles whose amino group is adjacent to the ring nitrogen [5].

It seemed of interest to us to study the reaction of 1-phenyl-3-aminopyrazoline with various β-dicarbonyl compounds with the objective of preparing derivatives of the five-membered-ring-hydrogenated system of 1-phenyl-pyrazolino-[2,3-a]-pyrimidine, which has not been described in the literature. The following reaction was envisaged:



(I) R′ = H, R″ = CH₃;
(II) R′ = H, R″ = OH;
(III) R′ = CH₃, R″ = OH;
(IV) R′ = C₆H₅, R″ = OH;

It was found that 1-phenyl-3-aminopyrazoline does enter into reaction with acetoacetic, malonic, methylmalonic, and ethylmalonic esters on heating without a solvent for an hour at 140-210° (depending on the nature of the dicarbonyl compound), and the products are the expected heterobicyclic compounds (I-IV) (see Table). At the same time the alcohol or the mixture of alcohol and water formed during the reaction is distilled off. The yield of reaction products, however, is very small due to serious resinification.

Compound	Reaction temp.	Yield, (%)	Melting point	Empirical formula	Found (%)		Calc. (%)	
					C	H	C	H
(I)	140—160°	5.7	194—196°	$C_{13}H_{13}ON_3$	67.84	6.25	68.72	5.73
(II)	170—190	2.1	199—200	$C_{12}H_{11}O_2N_3$	62.95	5.70	62.88	4.82
(III)	140—170	10.7	267—269	$C_{13}H_{13}O_2N_3$	63.52	4.40	64.19	5.35
(IV)	180—210	9.4	243—245	$C_{14}H_{15}O_2N_3$	63.94	6.07	65.36	5.83

The reaction either does not go in boiling ethyl, hexyl, and heptyl alcohols, glacial acetic acid, and quinoline, or leads to complete resinification. No effect is achieved by use as a catalyst of an alcoholic solution of sodium ethoxide or of an amine hydrochloride. Heterobicyclic products generally could not be obtained from acetylacetone, cyanoacetic ester, and substituted acetoacetic esters.

1-Phenyl-7-hydroxy-pyrazolino-[2,3-a]-pyrimidines do not contain a conjugated system of double bonds and apparently differ from carbazicondensed pyrazolo- and triazolopyrimidines in being amenable to formation only

under rather drastic conditions that are accompanied by resinification. Other preparative complications are the great difficulties in separation of the products and their final purification [6, 7].

Due to their amphoteric character our compounds (I-IV) are soluble in acids and alkalies. We did not carry out special verification of the relative positions of the methyl and hydroxy groups in compound (I). They follow from numerous investigations on the carbazicondensation: The carbethoxyl group of acetoacetic ester always reacts with the amino group, and the carbonyl group with the ring nitrogen of the aminoheterocycle [4, 7].

EXPERIMENTAL

General procedure for preparation of 1-phenyl-7-hydroxypyrazolino-[2,3-a]-pyrimidines. A mixture of 0.03 mole of 1-phenyl-3-aminopyrazoline [8] and 0.03 mole of β-dicarbonyl compound was heated for an hour at the temperature indicated in the table, and simultaneously the alcohol or mixture of alcohol and water was distilled off. The resinous reaction product was treated with absolute alcohol, and the solid residue was filtered and recrystallized several times from absolute alcohol. Yields, melting points, and analytical data are set forth in the table.

SUMMARY

Condensation of 1-phenyl-3-aminopyrazoline with acetoacetic, malonic, methylmalonic, and ethylmalonic esters gave derivatives of the previously undescribed heterobicyclic system 1-phenyl-7-hydroxy-pyrazolino-[2,3-a]-pyrimidine.

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All abbreviations of periodicals in the above bibliography are letter-by-letter transliterations of the abbreviations as given in the original Russian journal. *Some or all of this periodical literature may well be available in English translation.* A complete list of the cover-to-cover English translations appears at the back of this issue.

CATALYTIC CONDENSATION OF SCHIFF BASES FROM ESTERS OF p-AMINOBENZOIC ACID AND AROMATIC ALDEHYDES WITH FATTY-AROMATIC KETONES

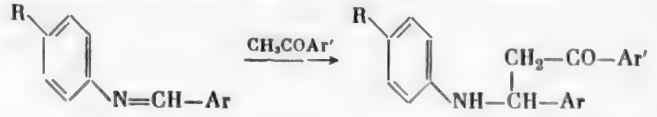
N. S. Kozlov and V. D. Pak

Translated from Zhurnal Obshchei Khimii, Vol. 31, No. 2,
pp. 497-499, February, 1961
Original article submitted March 28, 1960

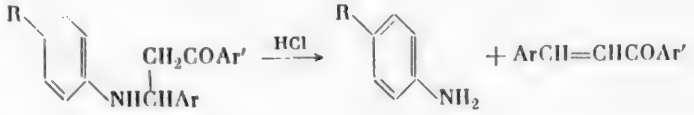
The catalytic condensation of Schiff bases with saturated and fatty-aromatic ketones was previously described [1-3]. Depending on the starting substances, the reaction gave β-arylaminoketones or derivatives of 2-phenyl-5,6-benzoquinone. Studies were also made of the condensation of Schiff bases (from methyl, ethyl, propyl, and butyl esters of p-aminobenzoic acid and benzaldehyde or anisaldehyde) with acetophenone and p-methoxyacetophenone [4].

In the present work we studied the condensation of the above Schiff bases with p-chloro- and p-bromoacetophenone. We synthesized chloro- and bromo derivatives of β-arylaminoketones containing the p-aminobenzoic acid residue: p-chlorophenyl-(β-p-carbomethoxyanilino-β-phenylethyl) ketone (I); p-chlorophenyl-(β-anesthesino-β-phenylethyl) ketone (II); p-chlorophenyl-(β-p-carbopropoxyanilino-β-phenylethyl) ketone (III); p-chlorophenyl-(β-p-carbobutoxyanilino-β-phenylethyl) ketone (IV); p-bromophenyl-(β-p-carbomethoxyanilino-β-phenylethyl) ketone (V); p-bromophenyl-(β-anesthesino-β-phenylethyl) ketone (VI); p-bromophenyl-(β-p-carbopropoxyanilino-β-phenylethyl) ketone (VII); p-bromophenyl-)β-p-carbobutoxyanilino-β-phenylethyl) ketone (VIII); p-chlorophenyl-(β-p-carbomethoxyanilino-β-p-methoxyphenylethyl) ketone (IX); p-chlorophenyl-(β-anesthesino-β-methoxyphenyl) ketone (X); p-chlorophenyl-(β-carbopropoxyanilino-β-p-methoxyphenylethyl) ketone (XI); p-chlorophenyl-(β-p-carbobutoxyanilino-β-p-methoxyphenylethyl) ketone (XII); p-bromophenyl-(β-p-carbomethoxyanilino-β-p-methoxyphenylethyl) ketone (XIII); p-bromophenyl-(β-anesthesino-β-p-methoxyphenylethyl) ketone (XIV); p-bromophenyl-(β-p-carbopropoxyanilino-β-p-methoxyphenylethyl) ketone (XV); p-bromophenyl-(β-p-carbobutoxyanilino-β-p-methoxyphenylethyl) ketone (XVI).

Synthesis of β-arylaminoketones can be regarded as the result of addition of a molecule of fatty-aromatic ketone to the azomethine bond of the Schiff base, which may be represented as follows:



The chemical character of the synthesized compounds was confirmed by their susceptibility to hydraminic cleavage: On heating with concentrated hydrochloric acid they broke down to amine and the corresponding chalcone:



EXPERIMENTAL

β-Arylaminoketones were synthesized by the procedure described earlier [4]. Results are set forth in the table. Hydraminic cleavage of the β-arylaminoketones was effected by the procedure described in [1].

No. of compound synthesized	R	R_1	R_2	Yield (%)	Melting point	% N	
						found	calc.
(I)	CH_3OCO	H	Cl	54.0	161—162°	3.55	3.73, 3.51
(II)	C_2H_5OCO	H	Cl	51.9	152—153.5	3.43	3.45, 3.72
(III)	C_3H_7OCO	H	Cl	57.3	131—132	3.32	3.24, 3.40
(IV)	C_4H_9OCO	H	Cl	46.9	132.5—133.5	3.21	3.36, 3.39
(V)	CH_3OCO	H	Br	53.6	176.5—177	3.19	3.15, 3.09
(VI)	C_2H_5OCO	H	Br	50.2	119.5—121	3.09	3.11, 3.18
(VII)	C_3H_7OCO	H	Br	63.0	134—135	3.00	2.95, 2.93
(VIII)	C_4H_9OCO	H	Br	45.8	137—138	2.91	3.16, 2.99
(IX)	CH_3OCO	OCH_3	Cl	59.1	141—142	3.30	3.07, 3.04
(X)	C_2H_5OCO	OCH_3	Cl	53.9	161—162	3.19	3.08, 3.08
(XI)	C_3H_7OCO	OCH_3	Cl	78.9	149—150	3.10	3.28, 3.25
(XII)	C_4H_9OCO	OCH_3	Cl	38.3	105.5—106.5	3.00	3.09, 2.95
(XIII)	CH_3OCO	OCH_3	Br	44.0	139—140	2.99	3.09, 3.03
(XIV)	C_2H_5OCO	OCH_3	Br	41.3	165—166	2.90	2.86, 2.86
(XV)	C_3H_7OCO	OCH_3	Br	40.8	159.5—160.5	2.82	2.93, 2.79
(XVI)	C_4H_9OCO	OCH_3	Br	36.0	122—123	2.74	2.86, 2.77

Hydraminic cleavage of compounds (I-IV) thus gave 4'-chlorochalcone with m.p. 101°; compounds (V-VIII) gave 4'-bromochalcone with m.p. 104-105°; compounds (IX-XI) gave 4-CH_3O-4'-chlorochalcone with m.p. 124°; compounds (XII-XVI) gave 4-CH_3O-4'-bromochalcone with m.p. 146°. The melting points of the chalcones isolated after hydraminic cleavage agree with the literature data [5].

According to these data [6] all of the chalcones prepared above were obtained from the appropriate aromatic aldehydes (benzaldehyde or anisaldehyde) and p-chloro- and p-bromoacetophenones.

No depressions of melting point were observed in mixed tests on the synthesized chalcones and those obtained by hydraminic cleavage.

SUMMARY

A study was made of the catalytic condensation of Schiff bases prepared from esters of p-aminobenzoic acid and aromatic aldehydes (benzaldehyde and anisaldehyde) with p-chloroacetophenone and p-bromoacetophenone.

A series of 16 β-arylaminoketones, not described in the literature, was synthesized.

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HERBICIDES AND PLANT GROWTH REGULATORS

XXXVI. SYNTHESIS OF SOME TETRACHLORO-, PENTACHLORO-, AND HEXACHLORO-3,6-ENDOMETHYLENETETRAHYDROPHTHALAMIC ACIDS AND THEIR IMIDES

N. N. Mel'nikov, L. G. Vol'fson, and S. D. Volodkovich

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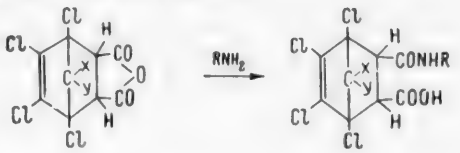
Original article submitted February 11, 1960

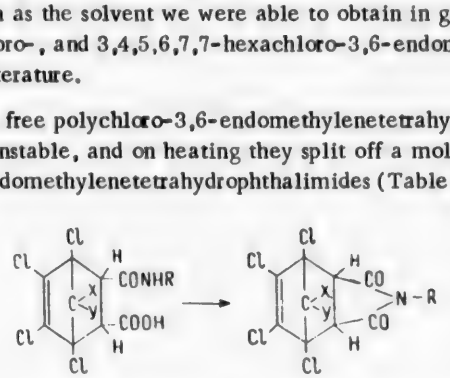
Sodium 3,6-endoxohexahydrophthalate [1] is well-known as an interesting defoliant and herbicide. Its action is apparently associated with displacement of physiologically important substances in the ferments of plant systems [2]. This hypothesis is supported in particular by the differing physiological activities of the endo- and exo-isomers. Various 3,6-endoxohexahydrophthalamic acids [3] and phthalamic acids [1, 4] have also been proposed in recent years as selective herbicides, and some of them find application in agriculture.

In connection with the study of the action of this class of substances, considerable interest is attached to the synthesis of various structurally similar compounds. In continuation of our earlier work [5, 6] on the synthesis of various derivatives of halo-3,6-endoxohexahydrophthalic acid, we undertook a study of tetrachloro-, pentachloro-, and hexachloro-3,6-endomethylenetetrahydrophthalamic acids, which are obtained with facility and in good yields by reaction of the corresponding anhydrides with amines.



This reaction proceeds nicely in any inert organic solvent incapable of reacting either with the amine or the anhydride. Using ether or dioxan as the solvent we were able to obtain in good yields a large number of 3,4,5,6-tetrachloro-, 3,4,5,6,7-pentachloro-, and 3,4,5,6,7,7-hexachloro-3,6-endomethylenetetrahydrophthalamic acids (Table 1) not described in the literature.

It should be noted that the free polychloro-3,6-endomethylenetetrahydrophthalamic acids, prepared from the primary amines, are relatively unstable, and on heating they split off a molecule of water with formation of the corresponding polychloro-3,6-endomethylenetetrahydrophthalimides (Table 2).



The poor stability of these compounds indicates that under our conditions there is no isomerization, and the synthesized compounds have a cis-structure.

EXPERIMENTAL

1. Initial substances. Tetrachloro-, pentachloro-, and hexachloro-3,6-endomethylenetetrahydrophthalic anhydrides were synthesized by reaction of maleic anhydride with 2,3,4,5-tetrachloro-, 1,2,3,4,5-pentachloro-, and 1,1,2,3,4,5-hexachlorocyclopentadienes, respectively. The initial anhydrides had the following melting points:

TABLE 1. Properties of Synthesized N-Alkyl(Aryl)-polychloro-3,6-endomethylenetetrahydrophthalamic Acids

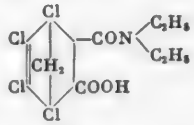
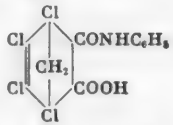
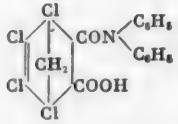
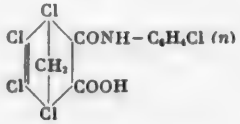
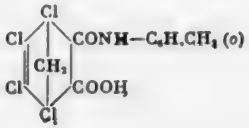
Radical at the nitrogen	Formula	Melting point	Yield (%)	M found	M calc.	Empirical formula	% N found	% N calc.	% Cl found	% Cl calc.
N-Alkyl(aryl)-3,4,5,6-tetrachloro-3,6-endomethylenetetrahydrophthalamic acids										
N,N-Diethyl		200°	83	—	—	$C_{13}H_{15}O_3NCl_4$	4.23, 4.16	3.74	37.36, 37.07	37.80
N-Phenyl		198—200 (with decomp.)	98	397.5	395	$C_{15}H_{11}O_3NCl_4$	3.77, 4.06	3.54	35.34, 35.30	35.94
N,N-Diphenyl		140—144	85	—	—	$C_{21}H_{15}O_3NCl_4$	2.88, 2.98	2.98	29.90, 29.99	30.14
N-p-Chlorophenyl		236 (с разл.)	90	444.4	429.5	$C_{15}H_{10}O_3NCl_5$	3.45, 3.41	3.25	40.60, 40.03	41.2
N-o-Tolyl		118—120	82	429	409	$C_{16}H_{13}O_3NCl_4$	3.76, 4.10	3.42	33.52, 33.08	34.65

TABLE 1 (Cont'd)

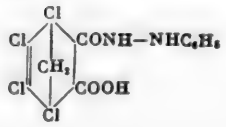
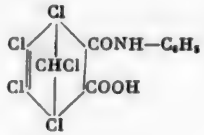
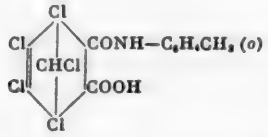
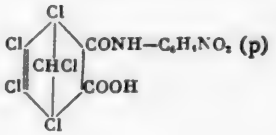
Radical at the nitrogen [e]	Formula	Melting point	Yield (%)	M found	M calc.	Empirical formula [a]	% N found	% N calc.	% Cl found	% Cl calc.
N-Aminophenyl		188	50	432	410	$C_{15}H_{12}O_3N_2Cl_4$	6.79, 6.79	6.82	34.53, 34.84	34.60
N-Alkyl(aryl)-3,4,5,6,7-pentachloro-3,6-endomethylenetetrahydrophthalamic acids										
N-Phenyl		125—126	100	425.5	429.5	$C_{15}H_{10}O_3NCl_5$	3.64, 3.66	3.60	41.03, 41.03	41.30
N-o-Tolyl		122—123	90	400	443.5	$C_{16}H_{12}O_3NCl_5$	3.07, 3.21	3.16	39.67, 39.18	40.02
N-p-Nitrophenyl		above 250 with decomp.	61	505	474.5	$C_{15}H_9O_5N_2Cl_5$	5.75, 6.15	5.90	35.72, 36.22	37.40

TABLE 1 (Cont'd)

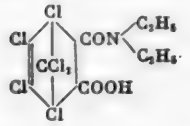
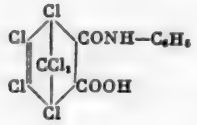
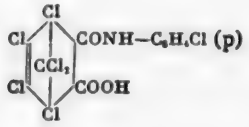
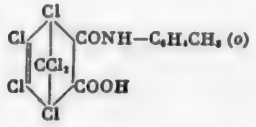
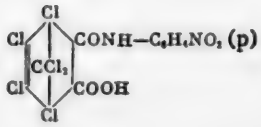
Radical at the nitrogen	Formula	Melting point	Yield (%)	M found	M calc.	Empirical formula	% N found	% N calc.	% Cl found	% Cl calc.
N-Alkyl(aryl)-3,4,5,6,7,7-hexachloro-3,6-endomethylenetetrahydrophthalamic acids										
N,N-Diethyl		142—143°	50	409	444	$C_{13}H_{13}O_3NCl_6$	3.17, 3.19	3.15	47.53, 47.65	47.9
N-Phenyl		125—126	100	506	464	$C_{15}H_9O_3NCl_6$	3.37, 3.33	3.01	44.35, 44.75	45.9
N-p-Chlorophenyl		123—124	100	506	498.5	$C_{15}H_8O_3NCl_7$	2.82, 2.89	2.81	49.15, 48.51	49.6
N-o-Tolyl		123—124	95	486	478	$C_{16}H_{11}O_3NCl_6$	3.18, 3.03	2.92	43.53, 43.66	44.5
N-p-Nitrophenyl		above 250° (with decomp.)	89	504.8	509	$C_{15}H_8O_5N_2Cl_6$	5.64, 5.36	5.48	41.08, 41.72	41.8

TABLE 2. Properties of Synthesized N-Alkyl(Aryl)-polychloro-3,6-endomethylenetetrahydrophthalimides

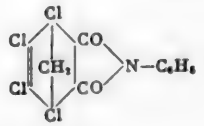
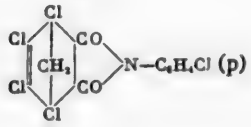
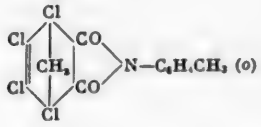
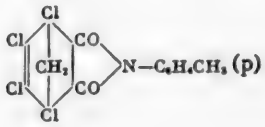
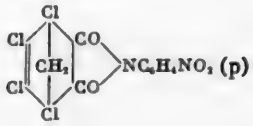
Radical at the nitrogen	Formula	Melting point	Empirical formula	% Cl	
				found	calc.
N-Alkyl(aryl)-3,4,5,6-tetrachloro-3,6-endomethylenetetrahydrophthalimides					
N-Phenyl		214—215°	$C_{15}H_9O_2NCl_4$	37.10, 37.57	37.6
N-p-Chlorophenyl		247—248	$C_{15}H_8O_2NCl_5$	42.35, 42.63	43.2
N-o-Tolyl		239--240	$C_{16}H_{11}O_2NCl_4$	36.35, 36.02	36.3
N-p-Tolyl		188—189	$C_{16}H_{11}O_2NCl_4$	36.30, 36.77	36.3
N-p-Nitrophenyl		266.5	$C_{15}H_8O_4N_2Cl_4$	34.01, 34.22	33.8

TABLE 2 (Cont'd)

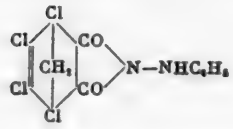
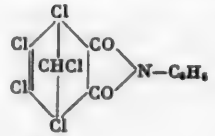
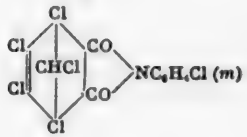
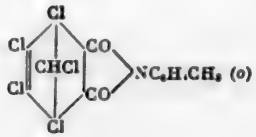
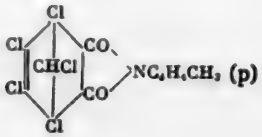
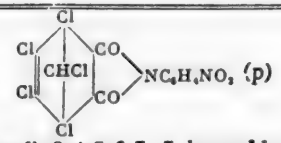
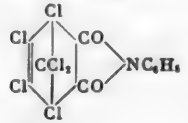
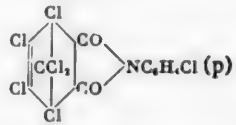
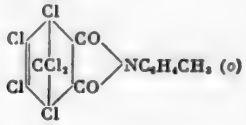
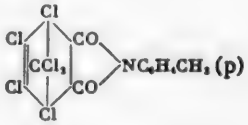
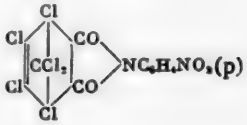
Radical at the nitrogen	Formula	Melting point	Empirical formula	% Cl	
				found	calc.
N-Aminophenyl		200°	$C_{15}H_{10}O_2N_2Cl_4$	36.02, 35.65	36.2
	N-Alkyl(aryl)-3,4,5,6,7-pentachloro-3,6-endomethylenetetrahydrophthalimides				
N-Phenyl		271	$C_{15}H_8O_2NCl_5$	42.27, 42.16	43.1
N-m-Chlorophenyl		263.5—264	$C_{15}H_7O_2NCl_6$	47.90, 48.43	47.4
N-o-Tolyl		244—245	$C_{16}H_{10}O_2NCl_5$	40.98, 41.68	41.7
N-p-Tolyl		285—286	$C_{16}H_{10}O_2NCl_5$	41.70, 41.88	41.7

TABLE 2 (Cont'd)

Radical at the nitrogen	Formula	Melting point	Empirical formula	% Cl found	% Cl calc.
N-p-Nitrophenyl		above 340	$C_{15}H_7O_4N_2Cl_5$	38.18, 38.44	38.9
N-Alkyl(aryl)-3,4,5,6,7,7-hexachloro-3,6-endomethylenetetrahydrophthalimides					
N-Phenyl		234	$C_{15}H_7O_2NCl_6$	47.71, 47.56	47.6
N-p-Chlorophenyl		257	$C_{15}H_6O_2NCl_7$	51.00, 51.93	51.4
N-o-Tolyl		185	$C_{16}H_9O_2NCl_6$	46.30, 46.16	46.3
N-p-Tolyl		225—227	$C_{16}H_9O_2NCl_6$	46.18, 45.95	46.3
N-p-Nitrophenyl		284—285	$C_{15}H_6O_4N_2Cl_6$	43.00, 42.99	43.3

3,4,5,6-tetrachloro-3,6-endomethylenetetrahydrophthalic anhydride 159-160°; 3,4,5,6,7-pentachloro-3,6-endomethylenetetrahydrophthalic anhydride 172-173°; 3,4,5,6,7,7-hexachloro-3,6-endomethylenetetrahydrophthalic anhydride 232-235°.

2. Reaction of polychloro-3,6-endomethylenetetrahydrophthalic anhydrides with amines. To a solution (cooled to 5°) of 0.02 mole of anhydride in 20-30 ml of dioxane or 100 ml of ether was added with good stirring an equimolar quantity of the amine. The reaction mixture was held at 5-15° for 15-40 min. In the case of 3,4,5,6-tetrachloro-3,6-endomethylenetetrahydrophthalic anhydride, crystals of 3,4,5,6-tetrachloro-3,6-endomethylenetetrahydrophthalamic acid came down immediately after addition of the amine. These crystals were filtered and recrystallized from isohexane or methanol. In the other cases a small quantity of methanol or isohexane was added to the reaction mixture, which was cooled to −10 to −15°. The deposited crystals were filtered and recrystallized from one of the solvents mentioned.

The compounds that we prepared and their properties are set forth in Table 1. All compounds were analyzed for nitrogen and chlorine contents, and were also titrated with aqueous-alcoholic sodium hydroxide in presence of phenolphthalein. It should be noted that even after gentle heating the compounds obtained from primary amines split off water, and neutral products are formed from the acid products.

3. Preparation of polychloro-3,6-endomethylenetetrahydrophthalimides. A weighed sample of acid was put into a porcelain dish and heated to the melting point. To the resulting melt was added methyl or ethyl alcohol. The deposited crystals were filtered, washed on the filter, well pressed, and dried in the air. Yields quantitative. All the imides synthesized in this way were analyzed for their chlorine content; their properties are set forth in Table 2.

SUMMARY

A series of new compounds was synthesized in the search for new herbicides and in connection with a study of the mechanism of their action on plants: 3,4,5,6-tetrachloro-, 3,4,5,6,7-pentachloro-, and 3,4,5,6,7,7-hexachloro-3,6-endomethylenetetrahydrophthalamic acids and their imides. It was shown that the acids are obtained in good yields by reaction of the corresponding anhydrides with amines, while the imides are obtained in good yields by brief heating of the respective acids.

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All abbreviations of periodicals in the above bibliography are letter-by-letter transliterations of the abbreviations as given in the original Russian journal. *Some or all of this periodical literature may well be available in English translation.* A complete list of the cover-to-cover English translations appears at the back of this issue.

A METHOD OF PREPARATION OF DIALKYLDITHIOPHOSPHONIC ACIDS

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Dialkyldithiophosphates $(RO)_2PSSH$ have recently acquired great importance. These acids are used in chemical industry as intermediates for the synthesis of many important insecticides; they are used as selective flotation reagents in the enrichment of ores of non-ferrous heavy metals and as a basis for preparation of high-grade additives to lube oils. Methods of preparation of dialkyldithiophosphates have been well worked out, and their properties have been closely studied.

Unlike the dialkyldithiophosphates, the dialkyldithiophosphonic acids R_2PSSH have been little studied, apparently because of the lack of convenient methods of synthesis.

Diethyldithiophosphonic acid, for example, was prepared [1] from the very difficultly accessible diethylphosphine by the following route:

$$3(C_2H_5)_2PH + 6S \longrightarrow (C_2H_5)_2P(S)SSSP(S)(C_2H_5)_2 + H_2S$$

$$(C_2H_5)_2P(S)SSSP(S)(C_2H_5)_2 \xrightarrow{(NH_4)_2S} (C_2H_5)_2PSSNH_4 \xrightarrow{H^+} (C_2H_5)_2PSSH$$

It was found [2, 3] that dialkyldithiophosphonic acids are formed together with other substances in the reaction of phosphorus pentasulfide with alkylmagnesium halides. Yields are 5-20% and the isolation of the pure substances is associated with great difficulties.

Preparation of dialkyldithiophosphonic acids by reaction of dialkyl thiophosphites with alkylmagnesium halides followed by addition of sulfur appeared possible to us.

$$(RO)_2P(S)H \xrightarrow{R'MgX} (R_2'PSMgX) \xrightarrow{S} (R_2'PSSMgX) \xrightarrow{H^+} R_2'PSSH$$

This synthesis would be analogous to the previously developed synthesis of dialkylthiophosphonic acids from dialkyl phosphites [4].

However the reaction of diethyl thiophosphite with butylmagnesium bromide and subsequent addition of sulfur went with formation of tetrabutyldithiodiphosphyl $(C_4H_9)_2P(S)P(S)(C_4H_9)_2$.

Tetrabutyldithiophosphyl is also formed if the diethyl thiophosphite is replaced by its sodium derivative. Potassium dibutyl thiophosphite reacts with a Grignard reagent to form a mixture of tetraalkyldithiodiphosphyl and dialkyldithiophosphonic acid.

$$(C_4H_9)_2PSK \xrightarrow{RMgX,\ S,\ H^+} R_2P(S)P(S)R_2 + R_2PSSH$$

However the yield of dithio acid is only about 30%.

We developed a method of synthesis of dialkyldithiophosphonic acids from dialkylmonothiophosphonic acids [4] by the following route:

$$R_2P(S)OH \xrightarrow{PCl_5} R_2P(S)Cl \xrightarrow{NaSH} R_2P(S)SNa \xrightarrow{H^+} R_2PSSH$$

R = C_2H_5, n-C_3H_7, iso-C_3H_7, n-C_4H_9 & $C_6H_5CH_2$

TABLE 1. Chlorides of Dialkylthiophosphonic Acids

Compound	Boiling point (pressure in mm)	n_D^{20}	d_4^{20}	MR_D found	MR_D calc.	% C found	% C calc.	% H found	% H calc	% P found	% P calc.	% Cl found	% Cl calc.	Yield (%)
$(C_2H_5)_2P(S)Cl$*	60—61°(4)	1.5281	1.1435	42.10	42.33	—	—	—	—	—	—	—	—	84.3
$(n\text{-}C_3H_7)_2P(S)Cl$**	73.5—74 (2.5)	1.5182	1.0859	51.53	51.56	—	—	—	—	—	—	—	—	96.8
$(iso\text{-}C_3H_7)_2P(S)Cl$	58.5—59 (2.5)	1.5232	1.0978	51.37	51.56	38.9, 38.8	39.0	7.7, 7.5	7.6	16.6, 16.7	16.8	19.1, 19.2	19.2	84.3
$(n\text{-}C_4H_9)_2P(S)Cl$***	84—85 (2)	1.5160	1.0570	60.76	60.80	45.0, 44.7	45.2	8.4, 8.2	8.5	14.7, 14.4	14.6	—	—	85.2
$(C_6H_5CH_2)_2P(S)Cl$	M.p. ...130.5—131.5°					—	—	—	—	11.0, 11.0	11.0	13.1, 13.0	12.6	91.0

*Literature data [5]: n_D^{20} 1.5294, d_4^{20} 1.1438.

**Previously prepared by us [4]: b.p. 107-109° (7 mm), n_D^{20} 1.5190, d_4^{20} 1.0845.

***Also prepared by the earlier method [4]: b.p. 89.5-91° (3 mm), n_D^{20} 1.5147, d_4^{20} 1.0575.

Two directions of the reaction of phosphorus pentachloride with dialkylmonothiophosphonic acids are theoretically conceivable:

$$R_2P(S)OH + PCl_5 \longrightarrow R_2P(S)Cl + POCl_3 + HCl \quad (A)$$

$$R_2P(O)SH + PCl_5 \longrightarrow R_2P(O)Cl + PSCl + HCl \quad (B)$$

It was found that this reaction proceeds smoothly with formation of phosphorus oxychloride and the corresponding thiochlorides in yields of 80-95%, i.e., according to scheme A. Constants of the products are set forth in Table 1.

Subsequent steps in the synthesis (action of sodium hydrosulfide on dialkylthiophosphonic chlorides and separation of the free acid) likewise proceed with high yield (70-90%).

Dialkyldithiophosphonic acids are colorless, mobile liquids; on standing they decompose with release of hydrogen sulfide. Their alkali salts are oxidized with facility, for example by iodine, with formation of disulfides:

$$R_2PSSH \xrightarrow{NaOH + I_2} R_2P(S)SSP(S)R_2$$

Dialkyldithiophosphonic acids add on acrylonitrile at the double bond:*

$$R_2PSSH + CH_2{=}CHCN \longrightarrow R_2P(S)SCH_2CH_2CN$$

Their sodium salts are alkylated by alkyl halides with formation of thioesters, for example:

$$R_2P(S)SNa + ClCH_2CH_2SC_2H_5 \longrightarrow R_2P(S)SCH_2CH_2SC_2H_5 + NaCl$$

Benzyl chloride reacts similarly.

The constants of the prepared acids and their transformation products are set forth in Table 2.

EXPERIMENTAL

Tetrabutyldithiodiphosphyl. To a solution of Grignard reagent (from 11.78 g of magnesium and 66.3 g of butyl bromide in 250 ml of ether) was added 23.13 g of diethyl thiophosphite in a nitrogen atmosphere with intensive stirring at such a rate that the mixture boiled gently. After the mixture had been heated for an hour on a water bath, 6.5 g of sulfur was added in small portions (the ether boiled), and the reaction flask was heated for another hour. Addition was then made, with cooling and intensive stirring, of 150 ml of hydrochloric acid (1 : 1). The ether layer was separated, the aqueous layer extracted with ether, and the

*We did not establish the sequence of addition. There are good reasons for assuming that the dithiophosphoryl group adds on in the β-position.

TABLE 2. Diethyldithiophosphonic Acids and Products of Their Transformations

Compound	Boiling point (pressure in mm)	n_D^{20}	d_4^{20}	Melting point of sodium salt	Equiv.		% C		% H		% P		Yield (%)
					found	calc.	found	calc.	found	calc.	found	calc.	
$(C_2H_5)_2P(S)SH$	68.5—69° (2.5)	1.5858	1.1306	122.5—124°	154.1, 153.8	154.2	22.6, 22.8*	22.6	6.7, 6.7	6.8	—	—	72.5
$(n\text{-}C_3H_7)_2P(S)SH$	91—91.5 (2)	1.5632	1.0691	87—89	181.4, 181.9	182.3	39.2, 39.1	39.5	8.1, 8.0	8.3	16.6, 16.8	17.0	69.4
$(iso\text{-}C_3H_7)_2P(S)SH$	76—76.5 (3)	1.5745	1.0877	153—154.5	182.2, 181.9	182.3	32.0, 31.8**	32.4	7.4, 7.3	7.3	—	—	89.2
$(n\text{-}C_4H_9)_2P(S)SH$	99—99.5 (2)	1.5481	1.0314	hygroscop.	210.7, 209.1	210.4	45.8, 45.7	45.7	9.2, 9.0	9.1	14.3, 14.5	14.7	78.0
$(C_6H_5CH_2)_2P(S)SH$	M.p. 132.5—133.5°	—	—	—	278.0, 278.3	278.4	60.8, 60.5	60.4	5.4, 5.3	5.4	10.8, 10.6	11.1	93.2
$(C_6H_5CH_2)_2P(S)SCH_2C_6H_5$	M.p. 111—112	—	—	—	—	—	68.7, 68.7	68.4	5.7, 5.7	5.7	8.3, 8.4	8.4	Quantiative
$(n\text{-}C_3H_7)_2P(S)SCH_2CH_2SC_2H_5$	117—118 (0.1)	1.5623	1.0685	—	—	—	44.5, 44.6	44.3	8.6, 8.5	8.6	1 .4 11.3,	11.4	97.8
$(iso\text{-}C_3H_7)_2P(S)SCH_2CH_2SC_2H_5$	122—123 (0.1)	1.5661	1.0787	—	—	—	44.9, 44.8	44.3	8.6, 8.6	8.6	11.3, 11.3	11.4	81.1
$(n\text{-}C_4H_9)_2P(S)SCH_2CH_2SC_2H_5$	126—127 (0.1)	1.5516	1.0631	—	—	—	48.7, 48.5	48.3	9.2, 9.2	9.1	10.5, 10.5	10.4	70.0
$[(n\text{-}C_3H_7)_2P(S)S]_2$	M.p. 80—81°	—	—	—	—	—	39.9, 40.0	39.8	7.8, 7.9	7.8	17.0, 16.8	17.1	Quantitative
$[(iso\text{-}C_3H_7)_2P(S)S]_2$	M.p. 101.5—102.5	—	—	—	—	—	40.1, 39.9	39.8	7.8, 7.9	7.8	16.7, 16.9	17.1	The same
$(C_6H_5CH_2)_2P(S)SCH_2CH_2CN$	M.p. 113—114	—	—	—	—	—	61.3, 61.5	61.6	5.2, 5.2	5.5	9.4, 9.7	9.3	84.6
$(iso\text{-}C_3H_7)_2P(S)SCH_2CH_2CN$	140—141 (2)	1.5566	1.0977	—	—	—	—		—		13.2, 13.2	13.2	83.0

* Analysis for $(C_2H_5)_2P(S)SNa \cdot 2H_2O$.

** Analysis for $(iso\text{-}C_3H_7)_2P(S)SNa \cdot H_2O$.

extracts dried over sodium sulfate. After the ether had been removed in vacuo, the residue crystallized. Two recrystallizations from aqueous methanol gave 12.62 g (about 47%) of tetrabutyldithiodiphosphyl; m.p. 72.5-73°. Literature data: m.p. 73-73.5° [6], 74° [7], 75° [8].

Found %: C 54.3, 54.2; H 10.3, 10.1. M (cryoscopically in benzene) 350.3, 348.7. $C_{16}H_{36}S_2P_2$. Calculated %: C 54.2; H 10.2. M 354.5.

Reaction of potassium dibutyl thiophosphite with propylmagnesium bromide. A solution of propylmagnesium bromide (from 4.86 mg of magnesium and 27.06 g of propyl bromide in 80 ml of ether) was added in a stream nitrogen, with intensive stirring, to potassium dibutyl thiophosphite (prepared from 21.02 g of dibutyl thiophosphite and 3.95 g of potassium in 150 ml of ether). Addition was made at such a rate that the mixture boiled gently. The mixture was heated for an hour, and 4 g of sulfur was added after cooling. The mixture (cooled with ice water) was decomposed by dilute (1 : 1) hydrochloric acid. The upper layer was separated, the lower layer extracted with ether, and the ether evaporated in vacuo. To the residue was added 50 ml of water and sodium carbonate until the reaction was weakly alkaline. The insoluble portion was extracted with ether, and the extract dried over sodium sulfate. Removal of the ether in vacuo followed by recrystallization of the residue from aqueous methanol gave 1.79 g (6%) of tetrapropyldithiodiphosphyl; m.p. 144-145°. The literature reports m.p. 145° [6, 7].

Found %: C 47.7, 48.0; H 9.5, 9.4. $C_{12}H_{28}S_2P_2$. Calculated %: C 48.3; H 9.4.

The aqueous solution was strongly acidified with hydrochloric acid and the dipropyldithiophosphonic acid was extracted with benzene. An ammonia stream was passed into the benzene solution of the acid which had been dried over sodium sulfate, the benzene was taken off in vacuo, excess of saturated nickel chloride solution was added to the residue, and the resulting nickel salt extracted with benzene. Removal of the benzene left 5.8 g (27.5%) of the nickel salt of dipropyldithiophosphonic acid in the form of blue-violet crystals with m.p. 149-149.5°. No depression of melting point in a mixed test with the salt obtained from the acid synthesized from dipropylthiophosphonic chloride.

Dibenzyldithiophosphonic acid. Reaction between benzylmagnesium chloride (from 4.09 g of potassium and 21.52 g of benzyl chloride in 80 ml of ether) and potassium dibutylthiophosphite (from 17.64 g of dibutyl thiophosphite and 3.28 g of potassium in 150 ml of ether) was performed as in the preceding experiment. After addition of 4 g of sulfur, heating for an hour, and cooling with ice water, the mixture was decomposed with 100 ml of hydrochloric acid (1 : 1). The ether layer was separated, the lower layer extracted with ether, and the combined extract dried over sodium sulfate. After removal of the ether in vacuo, the solid residue was recrystallized from ligroin (b.p. 50-70°) with addition of benzene. There was isolated 8.91 g (38.1%) of dibenzyldithiophosphonic acid with m.p. 132-133°. A mixture with the acid prepared by the general method described below melted at 132-133°.

Dialkylthiophosphonic chlorides. To a solution of 0.1 mole of dialkylmonothiophosphonic acid in three times the volume of anhydrous carbon tetrachloride was gradually added (with intensive stirring) 0.1 mole of phosphorus pentachloride. The mixture was heated for an hour on a water bath (35-45°), the easily volatile products removed in vacuo, and the residue washed twice with water, extracted with benzene, and dried over sodium sulfate. After removal of the benzene, the residue was distilled in vacuo (Table 1).

Dialkyldithiophosphonic acids. A stream of dry hydrogen sulfide was passed into a solution of sodium methoxide (from 0.21 g-atom of sodium in 80 ml of absolute methanol) until the gas ceased to be absorbed. The solution was heated on a water bath to the boil, and 0.1 mole of dialkylthiophosphonic chloride was gradually added with intensive stirring in a nitrogen stream. The mixture was heated under the same conditions for another 1.5 hr, cooled, and filtered from the precipitated sodium chloride. The filtrate was evaporated to dryness in vacuo, and the solid salt recrystallized from benzene (with addition of alcohol) until the melting point was unchanged. The pure salt was dissolved in a small quantity of water and the solution strongly acidified with hydrochloric acid. The precipitated dithio acid was extracted with benzene; the extract was dried over sodium sulfate, the benzene taken off, and the residue distilled in vacuo (Table 2). The following were also prepared:

Nickel salt of diethyldithiophosphonic acid, m.p. 140.5-141° (the literature reports 140.5° [1, 2]).

Nickel salt of dipropyldithiophosphonic acid, m.p. 149.5-150°.

Found %: C 34.1, 33.8; H 6.6, 6.6; P 14.6, 15.3; S 13.8, 14.5. $C_{12}H_{28}S_5P_2Ni$. Calculated %: C 34.2; H 6.7; P 14.7; S 13.9.

β-Cyanoethyl esters of dialkyldithiophosphonic acids. To a benzene solution of dialkyldithiophosphonic acid was added (with vigorous stirring) an equimolar quantity of acrylonitrile (slight heat generation). After heating for 1.5 hr on a water bath (60-65°), the benzene was taken off in vacuo, and the residue distilled in vacuo (in the case of the ester of diisopropyldithiophosphonic acid) or recrystallized from a mixture of benzene and ligroin, as in the case of the ester of dibenzyldithiophosphonic acid (Table 2).

Preparation of esters of dialkyldithiophosphonic acids. The dialkyldithiophosphonic acid was neutralized with 10% sodium hydroxide (to phenolphthalein) and an equimolar quantity of alkyl halide was added. The reaction mixture was stirred on a water bath (70°) for 1.5 hr, after which the organic layer was collected and the aqueous layer extracted with benzene. Drying over sodium sulfate and removal of the benzene in vacuo were followed by distillation of the residue in vacuo. The benzyl ester of dibenzyldithiophosphonic acid was purified by recrystallization from aqueous alcohol (Table 2).

Oxidation of dialkyldithiophosphonic acids. An aqueous solution of iodine in potassium iodide was added to a solution of 0.01 mole of the sodium salt of dialkyldithiophosphonic acid in 20 ml of water until the coloration did not disappear. The excess of iodine was removed by addition of thiosulfate solution, and the precipitate was filtered off. Recrystallization was carried out from alcohol. Yield of disulfides nearly quantitative (Table 2).

SUMMARY

1. Reaction of alkylmagnesium halides with dialkylthiophosphites followed by addition of sulfur is found to lead to tetraalkyldithiodiphosphyls.

2. Dialkyldithiophosphonic acids were synthesized by the following route: dialkylmonothiophosphonic acid → → dialkylthiophonic chloride → dialkyldithiophosphonic acid.

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INVESTIGATION OF THE REACTIVITY OF THE HYDROGEN ATOMS OF THE METHYLENE GROUP OF SOME AZOLIDINES

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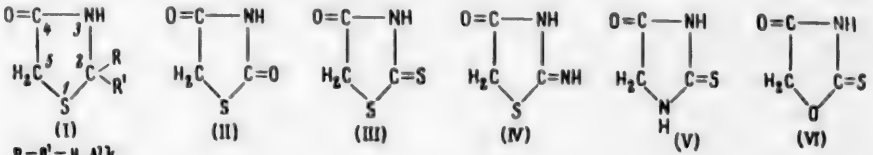
A large number of papers have recently been published on methods of synthesis of azolidines whose derivatives include such natural substances as penicillin, actithiazoic acid, and the antibiotic oxamycin. Some azolidines are employed in the synthesis of sensitizers and therapeutic agents (antithyroid preparations, spasmolytics, narcotics, analgesics), organic reagents for inorganic analysis, and as initial substances for the synthesis of complex aminoacids [1-6]. Investigation of the reactivity of individual atoms and groups in the molecule of 2-thio-4-thiazolidone (rhodanine) and of some of its analogs has been carried out by a number of workers [7, 8], but the relation between the mobility of the hydrogen atoms in the methylene group of 4-azolidones and the character of the heteroatom directly linked to the methylene group or the character of the substituent in the 2-position has not been studied.

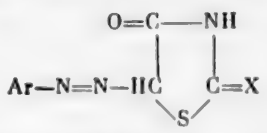
We have investigated the reactivity of the hydrogen atoms in the methylene group of 4-thiazolidone (I), thiazolidine-2,4-dione (II), 2-thio-4-thiazolidone (rhodanine) (III), 2-imino-4-thiazolidone (pseudothiohydantoin) (IV), 2-thiohydantoin (V), and 2-thiono-4-oxazolidone (VI).



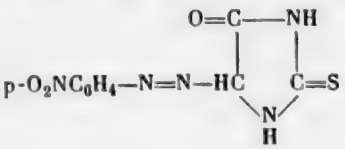
A partial positive charge is developed in 4-thiazolidones (I) under the influence of the electron-accepting carbonyl group at the carbon atom in the 5-position, and this enhances the reactivity of the hydrogen atoms in the methylene group. The electronegative sulfur atom directly linked to the methylene group has an unshared electron pair; it exerts a positive conjugation effect (+ C effect), weakens the positive charge induced in the carbon atom in the 5-position, and lowers the polarity of the C-H bond, so that the mobility of the hydrogen atoms in the methylene group is reduced.

Our previously prepared 4-thiazolidones (I) [9] are actually incapable of condensing with such an active carbonyl compound as p-dimethylaminobenzaldehyde, or with nitroso and diazo compounds. Replacement of the hydrocarbon radicals in the 2-position of a 4-thiazolidone by electronegative groups X = O, NH, S causes retention of electrons from the NH group at the 3-position, i.e., the $O=C-\overset{|}{NH}-\overset{|}{C}=X$ conjugation [10] is already dissipated and this leads to a higher polarity of the $-C=O$ bond, which in turn induces a higher positive charge on the carbon atom in the 5-position. An electronegative substitutent in the 2-position similarly influences the sulfur atom in the ring and thereby promotes polarization of the $-C-H$ bond in the methylene group, so that the mobility of the hydrogen atoms is increased.

Thiazolidine-2,4-dione (II), rhodanine (III), and pseudothiohydantoin (IV) actually undergo condensation with carbonyl compounds, nitroso compounds, and diazonium salts [11-14]. We thus prepared azothiazolidines:



(VII) Ar = p-$H_2NSO_2C_6H_4$, (VIII) Ar = p-$HO_3SC_6H_4$; a) X = NH, b) X = O, c) X = S*



(IX)

Replacement of the sulfur atom in the ring by the NH group, which under the influence of the electrophilic C = X group in the 2-position is less polarized than the sulfur atom, leads to diminution of the conjugation effect, i.e., the +C effect of the $-\overset{\curvearrowright}{NH}-C=\overset{\curvearrowright}{X}$ grouping is smaller than the +C effect of the $-\overset{\curvearrowright}{S}-C=\overset{\curvearrowright}{X}$ grouping. Due to the weakening of conjugation there is a greater weakening of the positive charge on the carbon atom in the 5-position than was the case when sulfur was present in the ring. A direct consequence of this must be a lowering of the mobility of the hydrogens of the methylene group in 2-thiohydantoin (V) in comparison with rhodanine (III).

According to the literature [15] 2-thiohydantoin (V) reacts rather sluggishly with aliphatic aldehydes, and our investigations showed that products of condensation at the methylene group could only be obtained with the simplest ketones and the most active diazonium salts (IX).

The molecule of 2-thiono-4-oxazolidone (VI) contains the more electronegative oxygen atom in the ring in place of the NH group, and therefore the shift of the unshared electron pair from the oxygen atom towards the thiono group is less marked than in the case of the NH group, so that the positive charge on the carbon atom in the 5-position is weakened to a greater extent and the mobility of the hydrogens in 2-thiono-4-oxazolidone (VI) must be smaller than in 2-thiohydantoin (V).

2-Thiono-4-oxazolidone actually only undergoes condensation with such active carbonyl compounds as aromatic aldehydes; our experiments showed that it does not condense with ketones, aliphatic aldehydes, and diazonium salts.

EXPERIMENTAL

Rhodanine [16] (III), 2-thiohydantoin (V), pseudothiohydantoin (IV), thiazolidine-2,4-dione [17] (II), 2-thiono-4-oxazolidone [18] (VI) were synthesized by the methods described in the literature.

5-(p-Sulfamidophenylazo)-thiazolidine-2,4-dione (VII b). A solution of 3.44 g of p-aminophenylsulfamide in 28 ml of 10% hydrochloric acid was cooled by addition of 9 g of ice. Diazotization was effected with 1.44 g of sodium nitrite dissolved in 2 ml of water. After 30 min the p-sulfamidophenyldiazonium solution was quickly poured into 25 ml of cooled 10% sodium hydroxide solution containing 2.5 g of 2,4-thiazolidinedione (II). After 0.5 hr the solution was acidified with hydrochloric acid, and the precipitated 5-(p-sulfamidophenyl)azothiazolidine-2,4-dione was filtered and washed with water. Yield of crude product 5.2 g (90%). Three recrystallizations from alcohol gave a red-orange powder with m.p. 245-248° (decomp.).

Found %: N 18.41. $C_9H_9O_4N_5S_2$. Calculated %: N 18.66.

The following substances were similarly prepared.

5-(p-Sulfamidophenylazo)pseudothiohydantoin (VIIa). Yield 85%. A red-orange powder (from alcohol), m.p. 262-264° (decomp.).

Found %: N 23.12, 23.24. $C_9H_9O_3N_6S_2$. Calculated %: N 23.41.

5-(p-Sulfophenylazo)thiazolidine-2,4-dione (VIII b); yield 68%; a red-orange powder with m.p. 271-274° (decomp.).

Found %: N 13.67, 13.71. $C_9H_7O_5N_3S_2$. Calculated %: N 13.95.

*We prepared these compounds earlier [5, 13].

5-(p-Sulfophenylazo)pseudothiohydantoin (VIIIa). A solution in the cold of 6.0 g of pseudothiohydantoin (IV) in 100 ml of 5% NaOH was prepared, and a suspension of p-sulfophenyldiazonium (prepared by the usual method of diazotization of 8.7 g of sulfanilic acid) was stirred in. The bright-red solution of the dye was stirred for an hour and then acidified with hydrochloric acid. The precipitate was filtered, washed with warm water, and recrystallized from alcohol. Yield 11.7 g (80%). An orange powder, m.p. 250-254° (decomp.). In an acidic aqueous alcoholic medium the color of the solution is yellow; in an alkaline medium it is bright-red.

5-(p-Nitrophenylazo)-2-thiohydantoin (IX). To a solution of 3.6 g of p-nitroaniline in 7 ml of hydrochloric acid (d 1.19) and 7 ml of water was added 25 ml of cold water. To the resulting suspension of p-nitroaniline was added a solution of 1.8 g of sodium nitrite in 6 ml of water. The solution of p-nitrophenyldiazonium salt was gradually run into a solution (cooled to 0°) of 2.9 g of 2-thiohydantoin (V) in 20 ml of pyridine. The solution quickly turned red, and after a short time it started to deposit a red precipitate. After the lapse of an hour part of the pyridine was distilled in vacuo, and the residual mass was poured into 0.1 N hydrochloric acid. The precipitate was filtered, washed with water, and dried. Yield 5.5 g (85%) of unpurified product. Recrystallization from alcohol gave a red powder with m.p. 290° (decomp.).

Found %: N 27.77, 27.68. $C_9H_7O_3N_5S$. Calculated %: N 27.92.

5-Isobutylidene-2-thiohydantoin. To a solution of 1.17 g of 2-thiohydantoin (V) in 10 ml of glacial acetic acid in presence of 1 g of anhydrous sodium acetate was added 0.88 g of methyl propyl ketone. The solution was boiled for 5 hr. After cooling, the crystals were twice crystallized from acetic acid containing active carbon. Fine, lustrous, yellow crystals, m.p. 198-200° (decomp.). Yield 1.2 g (64%).

Found %: N 15.54. $C_8H_{12}ON_2S$. Calculated %: N 15.21.

SUMMARY

1. The hydrogen atoms of the methylene group of 4-thiazolidones are incapable of undergoing condensation with active carbonyl compounds due to the influence of the sulfur atom in the ring and to the presence of the electron-donating NH group adjacent to the carbonyl group.

2. Introduction into the 2-position of 4-thiazolidone of electrophilic O, NH, or S groups considerably increases the mobility of the hydrogens of the methylene groups of thiazolidine-2,4-dione, rhodanine, and pseudothiohydantoin, which react with diazonium salts to form 5-azo compounds.

3. Replacement of sulfur in the ring of 2-thiono-4-thiazolidone by the more electronegative and less polarizable NH and O groups leads to decreased mobility of the hydrogens of the methylene group in the following sequence: rhodanine > 2-thiohydantoin > 2-thiono-4-oxazolidone.

4. Coupling of diazonium salts with pseudothiohydantoin, thiazolidine-2,4-dione, and 2-thiohydantoin gave five new dyes (azothiazolidines). These are orange or red substances, readily soluble in alkalies and changing color with the pH of the medium.

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ON THE REACTION OF N-CHLOROIMIDES OF CARBOXYLIC ACIDS WITH TRIALKYL PHOSPHITES, HALOPHOSPHITES, AND CYANOPHOSPHITES

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L. M. Chernushevich, and A. D. Kuntsevich

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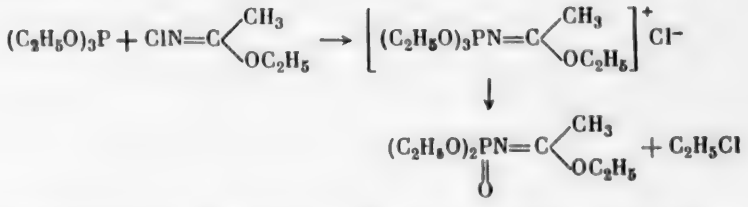
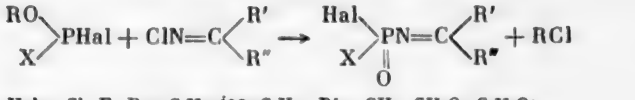
In a continuation of a work by one of us [1] the interaction of acetic and carbonic acid ester N-chloroimides with trialkyl phosphites, halophosphites, and cyanophosphites was studied. Contrary to chloroamines, sulfenyl chlorides, and alkyl hypochlorites, which react vigorously with phosphites in dilute solution in the cold, the reaction of ethyl N-chloroacetimide with triethyl phosphite goes quietly with slight evolution of heat; ethyl chloride is evolved only on prolonged heating at 60-70°, and the loss in weight reaches the theoretical value only on the fifth day. It must be presumed that the reaction takes place in two steps:



The phosphonium compound was not isolated in free form. A similar phosphonium compound was isolated earlier on treatment of triphenyl phosphite with diethylchloroamine [1].

Carbonic acid ester chloroimides react more vigorously with phosphites; the reaction should be carried out in a solvent with cooling, and subsequent heating for 2-3 hr at 40-50° in order to decompose the phosphonium compound. The main reaction products are esters of phosphoric acid dialkoxymethyleneamides.

Chloroamides react similarly with dialkyl chloro-, dialkyl fluoro-, alkyl dichloro-, and alkyl difluorophosphites, the reaction being carried out in ether or benzene and completed below room temperature; in this case the corresponding haloamidophosphates are obtained in yields from 27.5 to 70.5%.

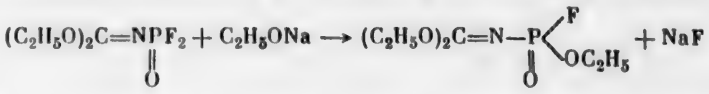


Hal = Cl, F; R = C_2H_5, iso-C_3H_7; R′ = CH_3, CH_3O, C_2H_5O;
R″ = CH_3O, C_2H_5O; X = Cl, F, OC_2H_5, iso-C_3H_7O.

Dialkyl fluorophosphites form rather stable phosphonium compounds with chloroimides. In the case of the reaction of diethyl fluorophosphite with ethyl N-chloroacetimide the active chlorine quickly disappears when the reagents are mixed, but the loss in weight of the mixture reaches the calculated value after heating for 7 hr at 80°. This fact is quite consistent with the idea of phosphonium compound formation. Let us note that prolonged heating of phosphonium compounds leads to a decrease in the yield of fluorophosphates. Hence after keeping for 1-2 hr at 40-50° the mixture was distilled in vacuo, and under these conditions the substances usually distilled within a range of one or two degrees.

Fluoroamidophosphates are thermally stable, and slowly hydrolyzed by water. In difluoroamidophosphates only one fluorine atom is hydrolyzed by aqueous alkali solutions in the cold; on treatment with the calculated

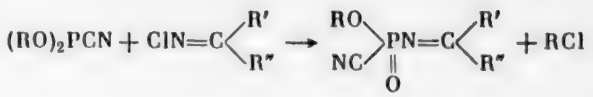
quantity of sodium ethoxide in a solvent the fluorine atom is replaced by an alkoxyl radical. The ethyl ester of fluorophosphoric acid diethoxymethylenamide was obtained by this method in 48% yield.



The constants of the substance are the same as those for the fluoroamidophosphate obtained by treating diethyl fluorophosphite with the chloroimide.

Contrary to fluoroamidophosphates, chloroamidophosphates are thermally unstable, can be distilled only in a high vacuum, and are relatively easily hydrolyzed by water at room temperature; on treatment of chloroamidophosphates with potassium cyanide in an aqueous medium at 5°, hydrolysis takes place together with replacement of chlorine by the cyano group. The ethyl ester of cyanophosphoric acid diethoxymethylenamide was obtained in about 20% yield by this method. We did not succeed in replacing the chlorine atom with a cyano group by heating with potassium cyanide in a chlorobenzene medium.

Cyanoamidophosphates were assumed, in the present work, to be obtained also by treatment of cyanophosphites with chloroimides. Earlier we showed that dialkyl cyanophosphites, like trialkyl phosphites and dialkyl halophosphites, can enter into an "Arbuzov rearrangement" with alkyl halides [2]. Cyanophosphites behave similarly on reaction with chloroimides:



Heat is evolved in the reaction; the yield of cyanoamidophosphates is 30-50%. Change in the reaction conditions has no substantial effect on the yield of cyanoamidophosphate.

Dicyanophosphoric acid dialkoxymethyleneamides are unstable substances; on keeping for a short time in a sealed ampule they decompose, gaseous products being evolved.

EXPERIMENTAL

Carboxylic ester N-chloroimides. The methyl and ethyl esters of N-chloroimidocarbonic acid were prepared by chlorinating an aqueous-alcoholic potassium cyanide solution in the presence of alkali [3]. N-Chloroimidoacetic acid esters were prepared by treating imidoacetic acid ester hydrochlorides with alkaline sodium hypochlorite solution [4]. The N-chloromethylacetimide was obtained in 58.8% yield.

B.p. 42° (60 mm), d^{20}_{20} 1.1112, $n^{21}D$ 1.4388.

Diethyl ester of phosphoric acid ethoxymethylmethylenamide. To 27.7 g of triethyl phosphite at room temperature, 20.3 g of N-chloroethylacetimide was added with stirring; in this case slight warming was observed. The mixture was heated at 50-70° for 5 days, until the loss in weight reached 11 g. On fractionation of the residue there was obtained 21.9 g of material with b.p. 106-111° (4 mm), containing about 5% chlorine; the chlorine-containing substances were removed by heating with alcohol in the presence of triethylamine; the amine hydrochloride was washed out with ice water.

B.p. 111-112° (5 mm), $d^{20.5}_{4}$ 1.0895, $n^{20.5}D$ 1.4405, MR 54.2; calc. 53.81.

Found %: P 13.59; N 6.48. $C_8H_{18}O_4NP$. Calculated %: P 13.9; N 6.28.

Diethyl ester of phosphoric acid diethoxymethylenamide. To 8.4 g of triethyl phosphite, 7.3 g of diethyl N-chloroimidocarbonate in 15 ml of benzene was added, the reaction mixture being cooled with ice water and stirred. Much heat was evolved in the reaction.

No ionic chlorine was found in the reaction mixture. The latter was heated at 40-50° for 2.5 hr, the benzene driven off in vacuo, and the residue fractionated. There was obtained 5.6 g (43%) of the substance.

B.p. 133-134° (1 mm), d^{20}_{4} 1.1400, $n^{18}D$ 1.4430.

Found %: N 5.68; P 12.9. $C_9H_{20}O_5NP$. Calculated %: N 5.54; P 12.25.

Reaction of dialkyl chlorophosphites with chloroimides (standard directions). To a solution of 0.11 mole of the dialkyl chlorophosphite in 50 ml of absolute ether, a solution of 0.1 mole of the chloroimide in 25 ml of ether or benzene was added, the reaction mixture being cooled with ice and salt, and stirred. The mixture was kept for 1 hr in the cold and 1 hr at room temperature. The solvent was distilled off in vacuo. The residue was a practically-pure chloroamidophosphate.

Reaction of dialkyl fluorophosphites with N-chloroimidocarbonic acid esters (standard directions). To 0.055 mole of the dialkyl fluorophosphite, a solution of 0.05 mole of the chloroimide in 15 ml of benzene was added, the reaction mixture being cooled with ice water. Much heat was evolved in the reaction. The mixture was kept for 2 hr at room temperature, until the loss in weight of the mixture reached the theoretical value. The solvent was driven off in vacuo, and the residue was fractionated.

Ethyl ester of fluorophosphoric acid ethoxymethylmethylenamide. A mixture of 5.15 g of diethyl fluorophosphite and 4.37 g of ethyl N-chloroacetimide was refluxed for 7 hr at 80°, until the weight loss was 2.1 g. After distilling twice, 4.5 g (63.5%) of the substance was obtained.

B.p. 86° (2.5 mm), d^{20}_4 1.1518, $n^{21}D$ 1.4015.

Found %: P 15.64; N 6.72; F 9.15. $C_6H_{13}O_3NPF$. Calculated %: P 15.74; N 7.11; F 9.64.

Isopropyl ester of fluorophosphoric acid ethoxymethylmethylenamide. To 9.5 g of diisopropyl fluorophosphite, 6.1 g of ethyl N-chloroacetimide was added, and the mixture was slowly heated to 50° and then fractionated in vacuo. There was obtained 2.9 g (27.5%) of the substance.

B.p. 74° (1.5 mm), d^{21}_4 1.1157, $n^{21}D$ 1.4200, MR 47.8; calc. 47.44.

Found %: P 14.07; F 8.28. $C_7H_{15}O_3NPF$. Calculated %: P 14.68; F 9.02.

Reaction of ethyl dichloro- and difluorophosphite with chloroimides. To a solution of 0.055 mole of the ethyl dihalophosphite in 25 ml of absolute ether, a solution of 0.05 mole of the chloroimide in 10 ml of ether or benzene was added, the reaction mixture being cooled with ice and salt, and stirred. Much heat was evolved in the reaction. The mixture was kept for 1 hr in the cold and 1 hr at room temperature, the solvent then distilled off in vacuo without heating above 30°, and the residue fractionated. Dichlorophosphoric acid diethoxymethylenamide is thermally unstable, and it partly decomposed on distillation in vacuo.

Reaction of difluorophospho(diethoxymethylenamide) with sodium ethoxide. To 2.9 g of difluorophospho(diethoxymethylenamide) was added sodium ethoxide solution (0.33 g of Na in 5 ml of anhydrous alcohol), the mixture was heated for 1 hr at 40-50°, the alcohol then driven off in vacuo, and the residue fractionated. There was obtained 1 g of the ethyl ester of fluorophosphoric acid diethoxymethylenamide. B.p. 120-122° (1 mm), $n^{19}D$ 1.4233.

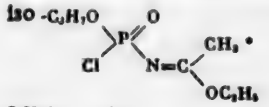
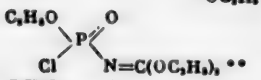
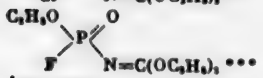
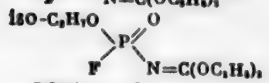
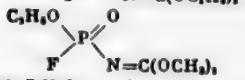
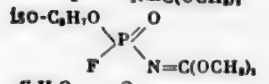
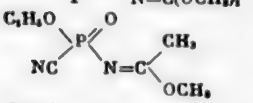
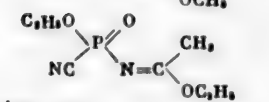
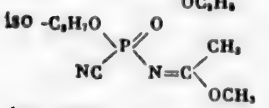
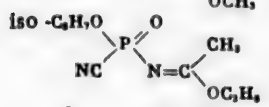
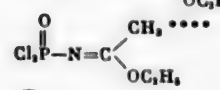
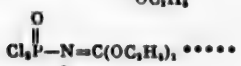
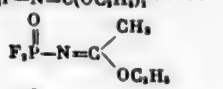
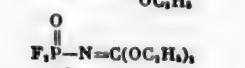
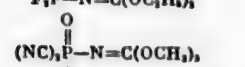
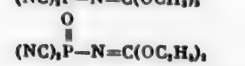
Found %: F 8.12, 8.20. $C_7H_{15}O_4NPF$. Calculated %: F 8.37.

Reaction of dialkyl cyanophosphites with alkyl N-chloroacetimides. To 0.02 mole of the dialkyl cyanophosphite, 0.02 mole of the alkyl N-chloroacetimide was added dropwise, the reaction mixture being cooled with ice water and stirred. A little heat was evolved in the reaction. The mixture was left for 1 hr at 18° and then heated for 30-40 min at 35-40° or, in the case of the reaction with diisopropyl cyanophosphite, 1.5 hr at 50-60°. The amidocyanophosphates were isolated from the mixture by distillation in vacuo.

Ethyl ester of cyanophosphoric acid diethoxymethylenamide. a) To a saturated aqueous solution of 7 g of potassium cyanide, 8 g of the ethyl ester of chlorophosphoric acid diethoxymethylenamide was added, the reaction mixture being cooled with ice water and stirred; the mixture temperature was kept below 10°; the mixture was stirred at this temperature for 80 min more, after which the water layer was separated, extracted with ether, and the extract combined with the oil layer. After drying over $MgSO_4$ and removing the ether, the extract was distilled. There was obtained 1.2 g (20%) of a substance with b.p. 143-146° (0.4 mm).

Found %: CN 10.50. $C_8H_{15}O_4N_2P$. Calculated %: CN 11.10.

b) To 2.5 g of diethyl cyanophosphite, a solution of 2.5 g of diethyl N-chloroiminocarbonate in 10 ml of absolute ether was added, the reaction mixture being cooled with water; the mixture was kept for 3 hr at room temperature. The ether was driven off and the residue fractionated in vacuo, fractions with b. p. 69-73 (5 mm), 76-78° (5 mm), and 141-145° (0.4 mm) (1.5 g) being isolated. From the first fraction the original N-chloroimide was

Compound	Molecular formula	Boiling point (pressure in mm)	d_4 (temp.)
	$C_7H_{14}O_3NPCl$	80—82° (0.2)	1.1600 (20)
	$C_7H_{15}O_4NPCl$	96—98 (0.5) with part. decomp.	1.2381 (20)
	$C_7H_{14}O_4NPF$	130—133 (3)	1.2050 (18)
	$C_8H_{17}O_4NPF$	129—131 (2)	1.1795 (20)
	$C_6H_{11}O_4NPF$	129—130 (4)	1.2917 (22)
	$C_6H_{13}O_4NPF$	134—135 (4)	1.2179 (21)
	$C_6H_{11}O_3N_2P$	108—110 (3)	1.1716 (21)
	$C_7H_{13}O_3N_2P$	105—107 (3) 88—90 (0.2)	1.1867 (19)
	$C_7H_{13}O_3N_2P$	94—95 (0.4)	1.1625 (20)
	$C_8H_{15}O_3N_2P$	98—100 (1.2) 91—94 (0.8)	1.1357 (20)
	$C_4H_8O_2NPCl_2$	78 (2.5)	1.3281 (22)
	$C_8H_{15}O_3NPCl_2$	86—90 (0.4)	1.2800 (20)
	$C_4H_8O_2NPF_2$	51 (7)	1.2501 (22)
	$C_8H_{15}O_4NPF_2$	92—94 (0.6)	—
	$C_8H_{12}O_3N_2P$	118—120 (3)	1.2260 (20)
	$C_7H_{10}O_3N_2P$	133—134 (2)	1.1806 (20)

• Found %: Cl 15.7. Calculated %: Cl 15.58.

•• Found %: Cl 14.69. Calculated %: Cl 14.58.

••• Found M 244.2. Calculated M 241.0.

•••• Found %: Cl 34.4. Calculated %: Cl 34.70.

••••• Found %: Cl 30.1. Calculated %: Cl 30.34.

n_D(temp.)	Yield (%)	% N		% P		% F		% CN		*MR*	
		found	calc.	found	calc.	found	calc.	found	calc.	found	calc.
1.4520 (20)	48.0	6.18	6.15	13.64	13.62	—	—	—	—	53.00	52.78
1.4520 (20)	—	6.24	5.75	—	—	—	—	—	—	54.00	54.05
1.4250 (18)	47.0	6.59	6.17	14.04	13.70	8.45	8.37	—	—	48.20	49.07
1.4290 (18.5)	45.0	5.73	5.81	—	—	7.65	7.88	—	—	—	—
1.4265 (20.5)	41.8	7.30	7.05	15.17	15.60	9.69	9.55	—	—	—	—
1.4242 (21)	63.5	6.54	6.56	14.14	14.50	8.81	8.91	—	—	45.50	44.47
1.4389 (21)	48.0	14.72	14.80	16.24	16.38	—	—	13.60	13.75	41.50	40.33
1.4520 (19)	51.0	13.50	13.70	15.13	15.20	—	—	12.60	12.75	46.30	44.95
1.4353 (20)	52.0	13.52	13.70	15.08	15.20	—	—	12.50	12.75	45.20	44.95
1.4435 (20)	46.0	12.72	12.85	14.13	14.21	—	—	—	—	50.80	49.57
1.4765 (22)	69.4	—	—	15.02	15.18	—	—	—	—	43.10	42.52
1.4715 (21)	30.0	6.94	6.03	14.88	13.45	—	—	—	—	—	—
1.3895 (22)	67.2	—	—	17.87	18.11	21.7	22.26	—	—	32.3	31.85
—	70.5	—	—	—	—	18.51	18.8	—	—	—	—
1.4435 (20)	40.0	—	—	—	—	—	—	26.9	27.8	39.90	37.98
1.4321 (20)	31.6	—	—	—	—	—	—	23.6	24.1	47.5	47.44

isolated; the second fraction contained 16.4% cyano group; this was possibly diethyl cyanophosphate or ethyl ethylcyanophosphonate; the third fraction was the ethyl ester of cyanophosphoric acid diethoxymethylenamide.

B.p. 144-145° (0.4 mm), d^{20}_4 1.1548, $n^{20}D$ 1.4750, MR 55.45; calc. 53.76.

Found %: CN 10.77, N 11.34; P 15.12. M 239. $C_8H_{15}O_4N_2P$. Calculated %: N 12.0; P 13.45; CN 11.10. M 234.

The ethyl ester of cyanophosphoric acid dimethoxymethylenamide was prepared under similar conditions in 35.3% yield.

B.p. 131-132° (0.55 mm), d^{20}_4 1.2056, $n^{20}D$ 1.4420, MR 44.60; calc. 44.54.

Found %: N 13.20; CN 12.20. $C_6H_{11}O_4N_2P$. Calculated %: N 13.64; CN 12.60.

Reaction of ethyl dicyanophosphite with carbonic acid ester N-chloroimides. To a solution of 0.01 mole of the N-chloroimide in 5 ml of absolute ether, 0.011 mole of ethyl dicyanophosphite was added, with stirring, at a temperature not over 35°. The ether was removed and the residue distilled in vacuo. In dicyanophosphates one cyano group was split off in the cold by 2 N alkali solution, whereas the second cyano group was split off only on boiling for 30 min.

The compounds obtained by the methods described above, are given in the table.

SUMMARY

The reaction of carboxylic ester N-chloroimides with trialkyl phosphites, as well as halo- and cyanophosphites, was studied.

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2. K. A. Petrov and A. A. Neimysheva. Zhur. Obshch. Khim. 29, 1827 (1959).
3. T. Sandmeyer, Ber. 19, 862 (1886).
4. J. Houben and E. Schmidt, Ber. 46, 3625 (1913).

All abbreviations of periodicals in the above bibliography are letter-by-letter transliterations of the abbreviations as given in the original Russian journal. *Some or all of this periodical literature may well be available in English translation.* A complete list of the cover-to-cover English translations appears at the back of this issue.

INVESTIGATIONS IN THE FIELD OF HYDROXY DERIVATIVES OF PHENANTHRENE

II. CERTAIN CONVERSION PRODUCTS OF THE BISULFITE COMPOUND OF 1,2-PHENANTHRO- (3',4')-FUROXAN

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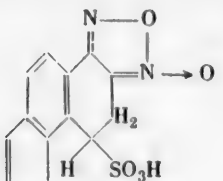
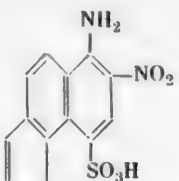
pp. 522-528, February, 1961
Original article submitted April 1, 1960

As noted earlier [1] the bisulfite compound of 1-nitroso-2-phenanthrol is converted by treatment with hydroxylamine to the bisulfite compound of 1,2-phenanthrenequinonedioxime. Oxidation of the latter with dilute nitric acid at 90-95° led to closing of the ortho-quinonedioxime grouping into a furoxan ring with formation of the bisulfite compound of 1,2-phenanthrofuroxan (I) and, as a by-product, 1,2-phenanthrofuroxan. Compound (I) is stable in neutral and acid media, but on brief treatment with boiling 1% soda solution it is converted to a mixture of 1-amino-2-nitrophenanthrene-4-sulfonic acid (II) and 1-hydroxy-2-nitrophenanthrene-4-sulfonic acid (III). These substances are the main reaction products, and their total yield exceeds 80%. Moreover, small amounts of 1,2-phenanthrofuroxan and 1,2-phenanthrofurazan are obtained. Compound (III) is a secondary reaction product, formed on alkaline hydrolysis of the amino group in compound (II).

Sulfonic acids (II) and (III) are unstable in an acid medium and go over to 1-amino-2-nitrophenanthrene (IV), and 1-hydroxy-2-nitrophenanthrene (V), respectively. The sulfo group is split off especially easily in the case of compound (II), whose sodium salt loses the sulfo group at room temperature in an aqueous solution acidified with acetic acid, or when its crystalline, hydrated form is heated above 130°. Hence great losses occur on isolation of sulfonic acid (II) from the reaction mixture, owing to the formation of amine (IV). On heating with sodium hydroxide solution, amine (IV) is converted to hydroxy compound (V).



(I)



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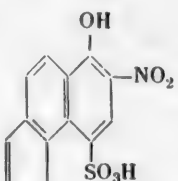

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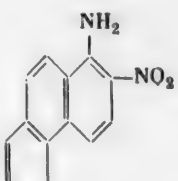

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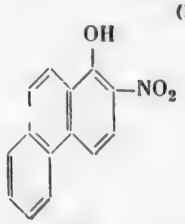

(V)

The reduction of compounds (III) and (II) led to 1-hydroxy-2-aminophenanthrene-4-sulfonic acid and 1,2-diaminophenanthrene-4-sulfonic acid, respectively, whereas the reduction of compounds (V) and (IV) led to 1-hydroxy-2-aminophenanthrene and 1,2-diaminophenanthrene, respectively. The latter was prepared also by reduction of 1,2-phenanthrenequinonedioxime and hydrolysis of the sulfo group in 1,2-diaminophenanthrene-4-sulfonic acid. The oxidation of 1-hydroxy-2-aminophenanthrene-4-sulfonic acid gave 1,2-phenanthrenequinone-4-sulfonic acid,

characterized in the form of p-toluidinium 1,2-dihydroxyphenanthrene-4-sulfonate, whereas acetylation of 1-hydroxy-2-aminophenanthrene gave the diacetyl derivative of 1-hydroxy-2-aminophenanthrene. The structure of product (III), and also, therefore, sulfonic acid (II), was proved by these two conversions.

Treatment of sulfonic acid (III) with 0.5 N nitric acid at 65-80° leads to a hydroxydinitrophenanthrene which is also obtained by direct nitration of hydroxy compound (V). Taking into account the fact that conversion of sulfonic acid (III) to the hydroxydinitro compound takes place under milder conditions than hydrolysis of the sulfo group in compound (III) or nitration of hydroxy compound (V), the intermediate formation of this last on nitration of sulfonic acid (III) seems unlikely.

The position of the second nitro group in the hydroxydinitrophenanthrene was not exactly determined, but presumably the dinitro compound has the structure of 1-hydroxy-2,4-dinitrophenanthrene.

Oxidation of 1,2-diaminophenanthrene and its 4-sulfonic acid by selenium dioxide led to the corresponding selenodiazoles. Besides, 1,2-diaminophenanthrene gave acyl derivatives, whereas the reaction with 9,10-phenanthrenequinone gave the corresponding azine.

The behavior of the bisulfite compound of 1,2-phenanthrofuroxan in soda solution is similar to the conversions of the bisulfite compounds of 1,2-naphthofuroxan, its 6-sulfo or 6-nitro derivative, and 1,2-anthrafuroxan [2]. On this basis the structure of the bisulfite compound of 1,2-phenanthrofuroxan may be represented by Formula (I).

EXPERIMENTAL

Bisulfite compound of 1,2-phenanthrofuroxan (I). Into a solution of 5.4 g of the bisulfite compound of 1,2-phenanthrenequinonedioxime in 135 ml of water, 60 ml of 57.4% nitric acid was poured; the mixture was heated to 90° and kept at 90-95° for 50 min. The 1,2-phenanthrofuroxan precipitate was filtered out (0.47 g, needles after crystallization from acetic acid, m.p. 221-222°) and sodium chloride (20% of the volume) added to the filtrate; the resulting precipitate of compound (I) was filtered out after 20 hr, and washed with sodium chloride solution and alcohol. Yield 4.32 g (72.7%).

The sodium salt of compound (I) consisted of yellowish needles (from alcohol), very slightly soluble in water and alcohol. The substance was stable in 80% sulfuric acid and hot 15% nitric acid.

Found %: C 42.53, 42.86; H 4.17, 3.96; N 7.26, 7.22; S 8.02, 8.12; H_2O 13.53 (dried at 120°). $C_{14}H_9O_5N_2SNa \cdot 3H_2O$. Calculated %: C 42.63; H 3.83; N 7.12; S 8.13; H_2O 13.76.

1-Amino-2-nitrophenanthrene-4-sulfonic acid (II). Into a boiling solution of 11.82 g of the sodium salt of compound (I) in 80 ml of water, 10 ml of 9% soda solution was poured all at once; the mixture was boiled for 4 min and quickly cooled. The yellowish precipitate was filtered out, and washed with water; weight, 0.18 g. On crystallization of this precipitate from acetic acid, 1,2-phenanthrofuroxan, m.p. 221-222°, and 1,2-phenanthrofurazan, m.p. 171-172°, were isolated.

The filtrate was acidified with acetic acid and sodium chloride (20% of the volume) added; the mixture was then kept at 18-20° for 4 days. The resulting precipitate of the sodium salt of sulfonic acid (II) and 1-amino-2-nitrophenanthrene was filtered out, and washed with sodium chloride solution and alcohol (precipitate a). The precipitate was boiled with 60 ml of water, and the aminonitrophenanthrene filtered out; weight 1.24 g (17.3%), m.p. 228-229°. Sodium chloride (15% of the volume) was added to the filtrate, and the precipitate of the sodium salt of (II), formed during 4 days, was filtered out, and washed with sodium chloride solution and alcohol (precipitate b); weight 3.21 g; on recrystallization of the precipitate from water, 2.81 g (26.1%) of the pure sodium salt of (II) was isolated.

When the sodium salt of (II) was salted out from an originally weakly alkaline solution, 1-amino-2-nitrophenanthrene was not formed, but the crystallization of (II) was hindered.

The sodium salt of (II) consisted of fine, red-orange prisms (from water), soluble in alcohol. It contained a molecule of water of crystallization, which was not removed at 130°. Solutions, acidified with acetic acid, deposited 1-amino-2-nitrophenanthrene slowly at ordinary temperatures and rapidly on heating.

On analysis for separable ammonia a solution of 0.4-0.5 g of the substance in 250 ml of water was alkalized with 25 ml of 40% sodium hydroxide solution and boiled until all the ammonia had been driven off; the latter was absorbed with acid.

Found %: C 46.88, 46.68; H 2.97, 3.08; N 7.83, 7.82. M 358.1 (from ammonia). $C_{14}H_9O_5N_2SNa \cdot H_2O$. Calculated %: C 46.92; H 3.09; N 7.81. M 358.3.

The diazo compound of amine (II) was prepared by adding compound (II) to a solution of sodium nitrite in concentrated sulfuric acid and pouring the mixture into ice water. Slightly soluble in water; formed an orange solution with resorcinol dissolved in aqueous soda, and a bluish-red solution with 2-naphthol-3,6-disulfonic acid so dissolved. After treatment with soda it combined only with resorcinol, a red-violet dye being formed.

A 2.5 g quantity of sodium carbonate was added to the filtrate from precipitates a and b, the solution boiled for 2 hr and acidified with hydrochloric acid, and the resulting precipitate filtered out, and recrystallized from water; 2.18 g (19.27%) of the sodium salt of (III) was obtained.

1-Hydroxy-2-nitrophenanthrene-4-sulfonic acid (III). A solution of 3.943 g of bisulfite compound (I) in a mixture of 200 ml of water and 20 ml of 10% soda was boiled for 1 hr, 30 ml of 27.7% sodium hydroxide was added, and the mixture was boiled until ammonia ceased to be driven off. The amount of the latter showed that the yield of the initially formed acid (II) was 89.5% (a small amount of 1,2-phenanthrofurazan distilled over with the ammonia).

The solution was acidified with hydrochloric acid and the resulting precipitate of the sodium salt of (III) filtered, and recrystallized from water; yield 3.06 g (81%), broad, yellow platelets (from water) soluble in alcohol.

Found %: C 44.60, 44.34; H 3.17, 3.12; N 3.89, 3.79; H_2O 9.55 (dried at 100-110°). $C_{14}H_8O_6NSN_a \cdot 2H_2O$. Calculated %: C 44.56; H 3.20; N 3.71; H_2O 9.54.

The disodium salt consisted of long, claret-red needles readily soluble in water.

The copper salt was prepared from the monosodium salt and copper sulfate; broad, yellow needles (from water) slightly soluble in water and readily in alcohol. Turned brown on drying, but reverted to yellow when wetted with water.

Found %: H_2O 13.45 (dried at 100-110°); Cu 7.85. $(C_{14}H_8O_6NS)_2 \cdot Cu \cdot 6H_2O$. Calculated %: H_2O 13.37; Cu 7.86.

1-Amino-2-nitrophenanthrene (IV). a) A mixture of 0.22 g of the sodium salt of (II) and 25 ml of 5% hydrochloric acid was brought to boiling, and the precipitated product (IV) was filtered out, and washed with water; yield 0.14 g.

b) A 0.7507 g quantity of the sodium salt of (II) was heated at 130-140° for 6 hr. The resulting product (IV) was washed with water. Yield quantitative.

Oranges needles (from acetic acid) slightly soluble in cold alcohol and cold acetic acid; m.p. 229-229.5°.

Found %: C 70.52, 70.41; H 4.18, 4.48; N 11.92, 11.92. $C_{14}H_{10}O_2N_2$. Calculated %: C 70.59; H 4.23; N 11.78.

1-Hydroxy-2-nitrophenanthrene (V). a) A mixture of 0.12 g of amine (IV) and 125 ml of 7% sodium hydroxide was boiled for 16 hr. The red sodium salt of (V) was converted to the free hydroxy compound (V) and the latter crystallized from alcohol; yield 0.10 g.

b) A solution of 0.37 g of the sodium salt of (III) in 15 ml of 0.5 N hydrochloric acid was heated to 80° for 10 min and then boiled for 30 min. The precipitate began to form only on boiling. The precipitate of product (V) was filtered out, and washed with water; yield 0.22 g (93.8%).

Yellow needles (from alcohol) insoluble in water and slightly soluble in alcohol; m.p. 159.5-160°.

Found %: N 5.93, 5.94. $C_{14}H_9O_3N$. Calculated %: N 5.85.

1-Hydroxy-2,x-dinitrophenanthrene. a) A solution of 0.37 g of the sodium salt of (III) in 15 ml of 0.5 N nitric acid was heated to 80° during 10 min and kept at 80° for 5 min. Separation of the dinitro compound began at 65°. The hydroxydinitrophenanthrene precipitate was filtered out, washed with water, and reprecipitated from soda solution; yield 0.2 g (71.8%).

b) A suspension of 0.07 g of nitro product (V) in 15 ml of 7.4% nitric acid was boiled for 7 hr. The precipitate was filtered out, and washed with water; yield 0.082 g (98.6%), m.p. 176.5-177° (decomp.). A mixture of the two hydroxydinitrophenanthrene samples melted at 177-177.2° (decomp.).

Fine, yellow needles insoluble in water and very slightly soluble in alcohol; m.p. 177-177.2° (decomp.).

Found %: N 9.89, 9.89. $C_{14}H_9O_5N_2$. Calculated %: N 9.86.

2-Amino-1-hydroxyphenanthrene-4-sulfonic acid. To a solution of 1.88 g of the sodium salt of (III) in 30 ml of water, 3 ml of 30% sodium hydroxide was added, followed by 2 g of aluminum dust during 20-25 min at 18-20°. The suspension was stirred for 40 min more, and filtered. The yellowish filtrate was acidified with hydrochloric acid, and the sulfonic acid precipitate which had formed after standing for a day was filtered out, and washed with water and alcohol; yield 1.14 g.

Colorless needles, gathered in bunches, insoluble in water and slightly soluble in alcohol.

Found %: C 56.08, 56.16; H 4.24, 4.46; N 4.69; S 10.50; H_2O 3.32 (dried at 110-120°). $C_{14}H_{11}O_4NS \cdot 0.5\ H_2O$. Calculated %: C 56.36; H 4.05; N 4.69; S 10.74; H_2O 3.19.

On treatment with sodium nitrite in the presence of copper sulfate a brown solution was formed, from which sodium chloride precipitated yellow needles of the diazo compound. The diazo compound was readily soluble in water; it formed a red-violet solution with resorcinol in a soda medium.

The aminohydroxysulfonic acid was oxidized to 1,2-phenanthrenequinone-4-sulfonic acid and p-toluidinium 1,2-dihydroxyphenanthrene-4-sulfonate prepared, as described for 1-amino-2-hydroxyphenanthrene-4-sulfonic acid [1]. The p-toluidine salt had m.p. 246-247° (decomp.); a mixture with known p-toluidinium 1,2-dihydroxyphenanthrene-4-sulfonate melted at 245.8-247.2° (decomp.).

2-Amino-1-hydroxyphenanthrene. To a solution of 0.72 g of nitrophenol (V) in 100 ml of alcohol, 15 ml of a 38.4% hydrochloric acid solution of stannous chloride was added; the mixture was boiled for 1 hr, 50 ml of alcohol was then driven off, and 10 ml of hydrochloric acid was added to the residue. The precipitated amino-compound hydrochloride was filtered out, and washed with alcohol; yield 0.67 g.

The hydrochloride consisted of colorless tablets (from alcohol) slightly soluble in water and more soluble in alcohol; m.p. 317-318° (decomp.).

Found %: N 5.66, 5.63; Cl 14.12, 14.23. $C_{14}H_{11}ON \cdot HCl$. Calculated %: N 5.70; Cl 14.44.

Diacetyl derivative of 2-amino-1-hydroxyphenanthrene. A mixture of 0.21 g of the aminohydroxy-compound hydrochloride and 10 ml of acetic anhydride was boiled for 2 hr and poured into water. The resulting precipitate was filtered out, and washed with water; yield 0.23 g. Fine, colorless tablets (from alcohol) soluble in acetic acid; m.p. 181-181.5°. (The diacetyl derivative of 1-amino-2-hydroxyphenanthrene consists of fine, colorless needles, m.p. 224.8-225.2° [1]).

Found %: C 73.77, 73.84; H 5.06, 5.21; N 4.77, 4.95. $C_{18}H_{15}O_3N$. Calculated %: C 73.90; H 5.15; N 4.77.

1,2-Diaminophenanthrene-4-sulfonic acid. To a solution of 3.58 g of the sodium salt of (II) in 60 ml of water 2 g of 30% sodium hydroxide was added, followed by 3 g of aluminum dust during 15 min at 18-20°. The suspension was stirred for 40 min more, filtered, and the yellowish filtrate acidified with hydrochloric acid. The precipitate was filtered out, washed with water and alcohol, and reprecipitated from sodium sulfite; yield 2.18 g. Light-brown prisms.

Found %: C 58.23, 58.26; H 4.24, 4.18; N 9.52, 9.77. $C_{14}H_{12}O_3N_2S$. Calculated %: C 58.31; H 4.19; N 9.71.

1,2-Phenanthro(3',4')-selenodiazole-4-sulfonic acid. To a suspension of 0.57 g of the diaminophenanthrene-sulfonic acid in 20 ml of water at 18-20°, a solution of 0.6 g of selenium dioxide in 2 ml of water was added, and the suspension was stirred for 14 hr. Four ml of 30% sodium hydroxide was added to the brown solution, and the resulting yellow selenodiazole precipitate was filtered out, and washed with water and alcohol; yield 0.7 g. The sodium salt consisted of yellow tablets (from water) slightly soluble in cold water and alcohol.

Found %: C 38.23, 38.35; H 3.19, 2.99; N 6.49, 6.66; H_2O 12.08 (dried at 120-125°). $C_{14}H_7O_3N_2SSeNa \cdot 3H_2O$. Calculated %: C 38.27; H 2.98; N 6.37; H_2O 12.30.

1,2-Diaminophenanthrene. a) A mixture of 2.38 g of 1,2-phenanthrenequinonedioxime, 100 ml of alcohol, and 15 ml of a 38.5% hydrochloric acid solution of stannous chloride, was boiled for 1 hr. The precipitate formed was filtered out, and washed with alcohol and ether; yield 2.31 g. The substance was purified by dissolving in alcohol and precipitating with hydrochloric acid.

b) A mixture of 1.27 g of nitroamine (IV), 80 ml of alcohol, and 10 ml of a 38.5% hydrochloric acid solution of stannous chloride was boiled for 1 hr. Further operations were performed as described above. Yield 1.23 g.

c) A mixture of 0.22 g of 1,2-diaminophenanthrene-4-sulfonic acid and 40 ml of 5% hydrochloric acid was boiled for 3 hr. The precipitate was filtered out, and washed with alcohol and ether; yield 0.20 g.

The dihydrochloride consisted of colorless, thick rhombic tablets readily soluble in alcohol and slightly soluble in water.

Found %: N 10.04, 10.02; Cl 25.31, 25.28; $C_{14}H_{12}N_2 \cdot 2HCl$. Calculated %: N 9.96; Cl 25.24.

Treatment with water converted it to the monohydrochloride. The latter consisted of colorless needles (from alcohol) readily soluble in alcohol and slightly soluble in water; m.p. 282-283° (decomp.).

Found %: C 68.82, 68.73; H 5.46; 5.37; N 11.58, 11.66. $C_{14}H_{12}N_2 \cdot HCl$. Calculated %: C 68.69; H 5.35; N 11.45.

The free base was obtained by treating an alcoholic solution of the dihydrochloride with sodium hydroxide. Colorless tablets (from alcohol) soluble in ether; darkened in air; m.p. 177-178° (decomp.).

Found %: N 13.23, 13.42. $C_{14}H_{12}N_2$. Calculated %: N 13.45.

Diacetyl derivative of 1,2-diaminophenanthrene. A mixture of 0.56 g of the diamine dihydrochloride, 0.35 g of anhydrous sodium acetate, and 10 ml of acetic anhydride was boiled for 3.5 hr and poured into water. The precipitate was filtered out, and washed with water; yield 0.52 g.

Fine, colorless needles (from 70% acetic acid) soluble in hot alcohol; m.p. 245.7-246.2°.

Found %: C 74.19, 74.02; H 5.53, 5.58; N 9.45, 9.62. $C_{18}H_{16}O_2N_2$. Calculated %: C 73.91; H 5.51; N 9.58.

Dibenzoyl derivative of 1,2-diaminophenanthrene. To a suspension of 0.14 g of the diamine dihydrochloride in 25 ml of water at 18-20°, 0.7 g of benzoyl chloride was added, followed gradually by 0.65 g of sodium carbonate, and the mixture was left for 24 hr. The precipitate formed was filtered out, and washed with water; yield 0.18 g.

Colorless needles (from acetic acid) soluble in alcohol; m.p. 268-269°

Found %: C 80.88, 80.74; H 4.79, 4.93; N 6.73, 6.65. $C_{28}H_{20}O_2N_2$. Calculated %: C 80.77; H 4.84; N 6.72.

1,2-Phenanthro-(3'-4')-selenodiazole. To a solution of 0.42 g of the diamine dihydrochloride in 100 ml of water, 5 g of selenium dioxide was added, and the precipitate formed was filtered out, and washed with water; yield 0.32 g.

Yellowish prisms (from acetic acid) soluble in alcohol; m.p. 189.8-190°.

Found %: C 59.05, 59.24; H 3.12, 3.15; N 10.02, 9.98. $C_{14}H_9N_2Se$. Calculated %: C 59.37; H 2.85; N 9.89.

1,2,3,4-Dibenzo-5,6-(1',2')-naphthophenazine. To a solution of 0.24 g of 1,2-diaminophenanthrene dihydrochloride in 50 ml of alcohol, a solution of 0.3 g of 9, 10-phenanthrenequinone in 100 ml of alcohol was added; the mixture was then boiled for 1 hr. The precipitate formed was filtered out, and washed with alcohol; yield 0.23 g.

Fine, yellow neddles (from benzene polychlorides), m.p. 299.5-300°; the substance was insoluble in cold alcohol and acetic acid, but gave a blue-violet solution in concentrated sulfuric acid.

Found %: C 88.14, 88.31; H 4.31, 4.43; N 7.33, 7.46. M 382 (cryoscopically in camphor). $C_{28}H_{16}N_2$. Calculated %: C 88.39; H 4.23; N 7.36. M 380.42.

SUMMARY

1. On oxidation with nitric acid, the bisulfite compound of 1,2-phenanthrenequinonedioxime is converted to the bisulfite compound of 1,2-phenanthrofuroxan.

2. The main conversion products of the bisulfite compound of phenanthrofuroxan in a soda medium are 1-amino- and 1-hydroxy-2-nitrophenanthrene-4-sulfonic acid.

3. In an acid medium 1-amino- and 1-hydroxy-2-nitrophenanthrene-4-sulfonic acid are converted to 1-amino- and 1-hydroxy-2-nitrophenanthrenes.

4. 1-Amino-2-nitrophenanthrene and its 4-sulfonic acid are converted by alkalis to the corresponding 1-hydroxy derivatives, whereas on reduction they give 1,2-diamino compounds. 1,2-Diaminophenanthrene also is formed on reduction of 1,2-phenanthrenequinonedioxime and on hydrolysis of 1,2-diaminophenanthrene-4-sulfonic acid.

5. The structure of the bisulfite compound of 1,2-phenanthrofuroxan is similar to those of the bisulfite compounds of 1,2-naphthofuroxan and 1,2-anthrafuroxan.

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All abbreviations of periodicals in the above bibliography are letter-by-letter transliterations of the abbreviations as given in the original Russian journal. *Some or all of this periodical literature may well be available in English translation.* A complete list of the cover-to-cover English translations appears at the back of this issue.

ALKYLATION AND ACYLATION OF ACETOACETIC AND MALONIC ESTERS IN THE PRESENCE OF COPPER POWDER

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In works of our laboratory it was shown that powders of various metals could be used as catalysts for the alkylation and acylation of the aromatic nucleus [1].

For the purpose of extending this method to aliphatic compounds we studied the condensation of acetoacetic and malonic esters with various halide compounds in the presence of copper in the present work.

Besides the classical methods of alkylation and acylation of β-dicarbonyl compounds by means of metallic sodium, several other variants are described. Syntheses have been carried out with magnesio- and zincoacetoacetic and malonic esters [2-6]. Spasov [7] used magnesium under conditions which precluded the formation of magnesioacetoacetic ester in acylation reactions. It proved possible even to use acid catalysts for replacement of methylene-group hydrogen in β-dicarbonyl compounds by alkyls and acyls. Condensations in the presence of BF_3 and $AlCl_3$ have been described [8, 9]. The mechanism of these reactions is considered analogous to that of Friedel-Crafts syntheses [8].

We carried out the condensations by heating (2-20 hr) a mixture of the reagents (an excess of ester was used) with a small quantity (0.08-0.3 mole) of copper powder per mole of halide. After a certain induction period hydrogen chloride evolution began.

In experiments with n-butyl bromide, tert-butyl chloride, allyl chloride, cyclohexyl chloride, and acetyl chloride (bromide) we were unable to isolate and to identify the expected products, although small yields of fractions having nearly the required boiling points were obtained.

The condensation of benzyl chloride with acetoacetic ester gave 10% of benzylacetoacetic ester. In the analogous reaction with malonic ester a little benzylmalonic ester and much greater quantities of ethanetetracarboxylic ester and toluene were obtained. In this case intermolecular transfer of hydrogen took place; this is often observed in alkylation reactions of aromatic compounds [10].

$$C_6H_5CH_2Cl + CH_2(COOC_2H_5)_2 \xrightarrow{-HCl} C_6H_5CH_2CH(COOC_2H_5)_2 + \\ + C_6H_5CH_3 + (C_2H_5OOC)_2CH{-}CH(COOC_2H_5)_2$$

Condensations with benzal chloride are much more easily carried out. A mixture of benzalacetoacetic ester and benzalacetone is obtained, the total yield being as much as 57%; benzalacetone usually predominates in the mixture. This condensation goes even at 85-90°, but it is appreciably faster at 100-120°. Higher temperatures (150-160°) lead to self-condensation of the benzal chloride [11].

Control experiments showed that without copper the condensation of acetoacetic ester with benzal chloride is possible only at 150-160°; it gives a low yield of products (10%).

The reaction of benzal chloride with malonic ester goes smoothly at 100-120° in the presence of copper. Yields of benzalmalonic ester reach 64%. In this way benzalacetophenone (75%) was easily prepared from benzal chloride and acetophenone.

The benzoylation of acetoacetic ester goes slowly on heating in a water bath (yield 22% after 12 hr). At 150-160° hydrogen chloride evolution ceases within 3 hr. There is obtained 40% of benzoylacetoacetic ester; part of the benzoyl chloride is converted to benzoic acid. At still higher temperatures (170-180°) and a greater quantity of copper (0.03 mole) the yields decrease, much benzoic acid being formed. Similar results are obtained with p-nitrobenzoyl chloride. At 100-120° the yield of p-nitrobenzoylacetoacetic ester is 43%.

In these two cases acetoacetic ester also is acylated without catalyst, but only at 160-180°; the acyl derivatives are obtained in 10-15% yields.

The benzoylation of malonic ester gave very small yields of benzoylmalonic ester; most of the benzoyl chloride was converted to benzoic acid.

EXPERIMENTAL

Benzyl chloride and acetoacetic ester. A mixture of 25 ml of benzyl chloride, 60 ml of acetoacetic ester, and 0.7 g of copper powder (GOST 4451-54) was refluxed in a flask at 140-160° for 6 hr. The copper became coated with a white layer of cuprous chloride. When the heating was stopped, hydrogen chloride evolution had nearly ceased; after this the liquid was left to stand, decanted, and fractionated. There were isolated: 40 ml of a mixture of the starting materials, b.p. 60-100° (14 mm); 2 g of an intermediate fraction with b.p. 115-150° (10 mm); 6.5 g (10%) of benzylacetoacetic ester, b.p. 156-170° (10 mm) [12]; 2 g of residue.

Benzylacetoacetic ester was ketonically cleaved by heating with water in a sealed tube at 180-190° for 18 hr [13]. Benzylacetone was obtained; it gave an oxime with m.p. 82-83° [13].

Benzyl chloride and malonic ester. Twelve g of benzyl chloride, 35 ml of malonic ester, and 0.5 g of copper powder prepared from copper sulfate by reduction with zinc dust [14] were gently boiled (160-170°) for 12 hr. Hydrogen chloride was rapidly evolved, and appreciable amounts of cuprous chloride accumulated.

On distillation of the reaction mixture there were isolated: a) 2 g of a fraction with b.p. 110-115° (730 mm) in which the presence of toluene was proved by preparing 2,4-dinitrotoluene, m.p. 70°, which gave no melting-point depression with a known sample; b) 2 g of a fraction with b.p. 155-165° (10 mm) in which the presence of benzylmalonic ester was proved by hydrolysis with alcoholic alkali [15]; benzylmalonic acid, m.p. 117°, was isolated, and identified by a mixture test with a known sample; c) 5 g of a fraction with b.p. 180-200° (10 mm); on hydrolysis with alcoholic alkali a mixture of acids was obtained, from which, by recrystallization from water, succinic acid (m.p. 185°) and a little ethanetetracarboxylic acid [m.p. 168° (decomp.)] were isolated. Both acids were identified by the absence of a melting point depression on mixing with samples of known acids.

Benzal chloride and acetoacetic ester. Forty ml of acetoacetic ester, 16 g of benzal chloride, and 0.3 g of copper were heated for 4 hr at 100-120°. Hydrogen chloride evolution was very rapid at first, but had nearly ceased at the end of the experiment.

Fractions isolated: a) 3 ml of a mixture of the starting materials, b.p. 80-110° (17 mm); b) 7.6 g (52%) of benzalacetone, b.p. 148-153° (15 mm) [16]; we prepared the 2,4-dinitrophenylhydrazone (m.p. 220-221°) and the oxime (m.p. 115° [17]); c) 1 g (5%) of benzalacetoacetic ester, b.p. 180-190° (17 mm); on redistillation it had b.p. 180-181° (18 mm); with hydroxylamine it gave an isoxazolone with m.p. 140-141° [18].

Benzal chloride and malonic ester. A mixture of 30 ml of malonic ester, 16 g of benzal chloride, and 0.5 g of copper was heated for 10 hr at 100-120°. On fractionation 16 g (64%) of benzalmalonic ester, b.p. 140-146° (5 mm) [19], was isolated. On hydrolysis with barium hydroxide solution, benzalmalonic acid, m.p. 192° [19], was obtained; it gave no melting-point depression in a mixture test with a known sample.

Benzal chloride and acetophenone. From 16 g of benzal chloride, 16 g of acetophenone, and 0.5 g of copper, heated for 5 hr at 120-130°, 15 g (75%) of benzalacetophenone, b.p. 185-190° (5 mm), m.p. 57° [20], was obtained; semicarbazone m.p. 167°.

Benzoyl chloride and acetoacetic ester. The condensation was carried out with 40 ml of acetoacetic ester, 12 ml of benzoyl chloride, and 0.5 ml of copper at 150-160° during 3 hr. On distillation 1.2 g of benzoic acid (m.p. 122°) and 9.1 g (40%) of benzoylacetoacetic ester, b.p. 180-190° (17 mm) [21], were isolated. For identification the latter was converted to benzoylacetic ester [22], and acetophenone obtained therefrom [23]; 2,4-dinitrophenylhydrazone, m.p. 237°.

p-Nitrobenzoyl chloride and acetoacetic ester Twenty ml of acetoacetic ester, 9.25 g of p-nitrobenzoyl chloride, and 0.20 g of copper were heated for 5 hr at 100-120°. There was obtained 6 g (43%) of p-nitrobenzoylacetoacetic ester, b.p. 180-190° (25 mm), m.p. 53° [24]. It was identified by cleavage to p-nitroacetophenone, m.p. 83-85° [23].

SUMMARY

The possibility of carrying out alkylation and acylation reactions of acetoacetic and malonic esters in the presence of copper powder has been shown. Yields of condensation products (40-75%) are close to those obtained by other, more laborious, methods.

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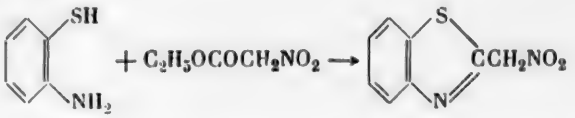
CONDENSATION ON NITROACETIC ESTER WITH o-AMINOPHENYLMERCAPTAN

A. I. Kiprianov and T. M. Verbovskaya

Institute of Organic Chemistry, Academy of Sciences, Ukr.SSR
Translated from Zhurnal Obshchei Khimii, Vol. 31, No. 2,
pp. 531-537, February, 1961
Original article submitted March 14, 1960

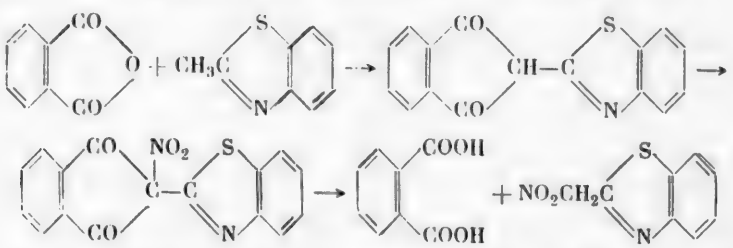
By heating an equimolecular mixture of nitroacetic ester and o-aminophenylmercaptan, A. I. Kiprianov and E. D. Smaznaya-Il'ina have obtained, with a 74% yield, a yellowish crystalline product melting at 273° (dec.) [1]. On the basis of the ability of carboxylic acid esters to condense with o-aminophenylmercaptan giving benzothiazole derivatives [2], as well as on the grounds of the analytical results given by the new product and some of its reactions, the authors have ascribed to the compound they synthesized the structure of a 2-methylbenzothiazole, and proposed the following scheme for its formation:



The substance melting at 273° dissolved in alkalies, and was reprecipitated unchanged by addition of acids to its alkaline solutions. Its sodium salt, and its acetyl, benzoyl, methyl, and ethyl derivatives were prepared and analyzed. It was shown that the substance undergoes methylation by the action of methyl iodide on its sodium salt, the methyl group not being attached to the nitrogen atom of the thiazole ring.

It was noticed at the same time that some other properties of the condensation product of o-aminothiophenol with nitroacetic ester cannot be easily reconciled with the proposed structure. Thus, the substance could not be reduced to the known 2-aminomethylbenzothiazole [3], and it did not condense with aldehydes. The high melting point and the extremely low solubility of the "nitromethylbenzothiazole" in organic solvents were also unexpected.

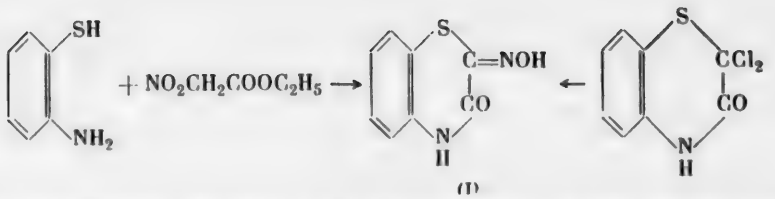
Later, L. P. Zalukaev and E. V. Vanag [4], while developing their method of preparation of 2-nitromethyl derivatives of nitrogen heterocycles, succeeded to synthesize 2-nitromethylbenzothiazole from 2-methylbenzothiazole through the corresponding nitrophthalone according to the following scheme:



The product obtained in this reaction melted at 120-130° (dec.). Its structure was unequivocal, as it was synthesized according to a general method, and upon hydrolysis with dilute sulfuric acid it gave 2-benzothiazole carboxylic acid.

Therefore, it became clear that the reaction product of nitroacetic ester with o-aminophenylmercaptan has been given a wrong structure.

As a result of a careful investigation of this reaction, we established that the reaction product is actually the 2-oxime of 2,3-diketodihydrobronzo-1,4-thiazine (I), which can also be prepared by the action of hydroxylamine on the known [5] dichloride.



(I)

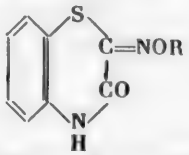
The products obtained were identified by the absorption spectra of their alcoholic solutions, and by their melting points.

During the work done for the elucidation of the structure of the compound under investigation, we made a complementary study of its properties, and we prepared some of its derivatives and analogs.

As already mentioned in the first study [1], the oxime (I) dissolves in alkalies. Cooling of its solution in hot 20% sodium hydroxide leads to the separation of its sodium salt. Its potassium salt separates out as yellowish platelets sparingly soluble in water upon cooling a solution of the oxime in aqueous-alcoholic potassium hydroxide solution.

The alkali metal salts of the oxime are very stable. Upon heating with a 10% potassium hydroxide solution in a sealed tube at 150° for 10 hr, a part of the oxime decomposes with the formation of ammonia and potassium carbonate, but a considerable part of the substance remains unchanged. The stability of the alkali metal salts of the oxime is also proved by the fact that the exchange of the alkali metal for a methyl group upon the action of dimethyl sulfate or methyl iodide requires heating with the methylating agent for several hours at a temperature above 100°. The stability of the alkali metal salts is apparently due to the occurrence of conjugation in their anion (see the following drawing).

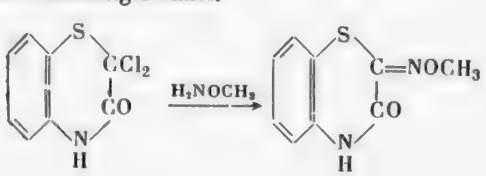
The oxime is also fairly stable toward the action of acids. It is soluble in concentrated sulfuric acid with the formation of a yellow conjugated cation (see drawing).



The oxime is precipitated unchanged by dilution of its solution in cold sulfuric acid with water; however, if the solution is heated before dilution with water, no precipitate is formed. When the substance was heated at 150° for 10 hr in a sealed tube with 30% sulfuric acid, a part of it was recovered unchanged, while the remaining part was transformed into benzothiazole and carbon dioxide. The isomerization of 2,3-diketodihydrobenzo-1,4-thiazine to benzothiazole-2-carboxylic acid has been studied by Zahn [5].

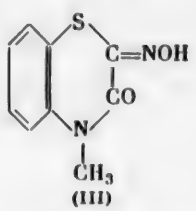
It was not possible to isolate the reduction products of the oxime (I). Prolonged boiling of the oxime with zinc dust and concentrated hydrochloric acid with the addition of alcohol gradually brings it into solution. However, we were able to isolate from this solution only a small amount of benzothiazole, which is the product of the hydrolysis of the oxime and of the isomerization of the dione first formed.

Methylation of the oxime (I) can be effected by heating its potassium salt with dimethyl sulfate in xylene. This leads to the substitution of the hydrogen atom of the oxime group, compound (II, R = CH_3) being formed. The latter can also be synthesized in the following manner:

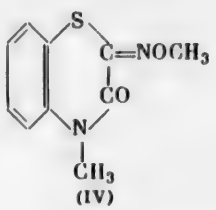


Product II is still capable of forming salts by reaction with alkalies.

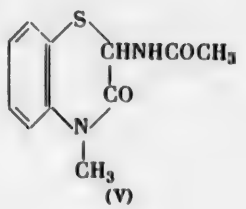
The acetyl derivative of the oxime (I) was obtained by refluxing this substance with acetic anhydride, and its benzoyl derivative by heating it with benzoyl chloride in pyridine.



(III)

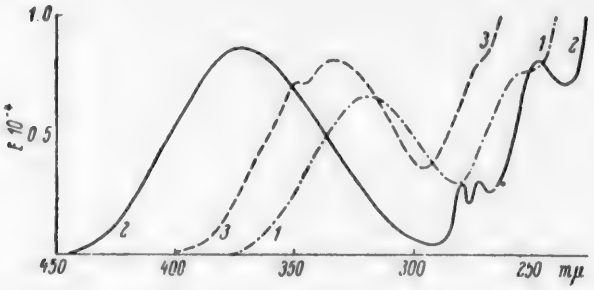


(IV)



(V)

Similarly to o-aminophenylmercaptan, N-methyl-o-aminophenylmercaptan condenses with nitroacetic ester. The product of this reaction is the oxime (III), giving yellowish crystals with m.p. 250°, which are somewhat more soluble than the oxime (I). Oxime (III) also gives acetyl and benzoyl derivatives. Its sodium salt reacts with dimethyl sulfate to give a dimethyl derivative (IV), which does not dissolve in alkalies, and which is identical to the product we prepared by heating the sodium salt of (II) with methyl iodide.



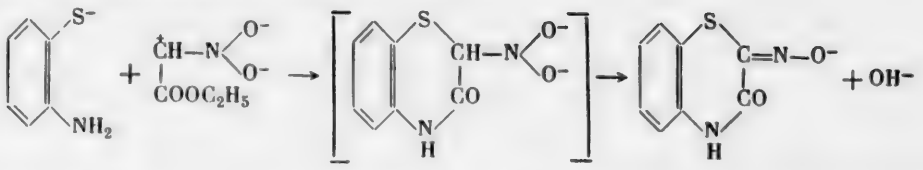
Absorption spectra of solutions of the 2-oxime of 2,3-diketodihydrobenzo-1,4-thiazine (I). 1) In alcohol; 2) in a mixture of sulfuric acid (90%) and alcohol (10%); 3) in 4% alcoholic potassium hydroxide.

Oxime (III) was reduced with tin and hydrochloric acid to an amine which was isolated as its acetyl derivative (V) melting at 159°. We prepared the same product by the reaction of ammonia with 2-chloro-3-keto-4-methyldihydrobenzo-1,4-thiazine.

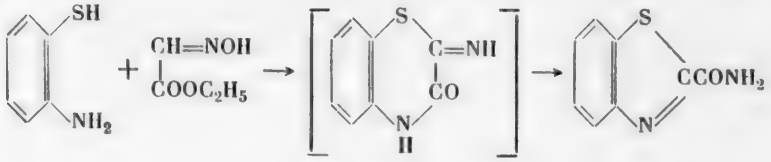
Our observations on the condensation reaction of o-aminophenylmercaptans with nitroacetic ester allow us to make a few assumptions concerning the mechanism of this reaction.

The fact that cyclization proceeds with the closure of a thiazine, and not a thiazole ring shows that the reaction starts with the addition of the mercapto group to the double bond of the isonitro form of the nitroacetic ester, which is apparently gradually formed during the heating of the reaction mixture. This assumption is confirmed by the fact that this reaction is promoted by alkalies. The cyclization which requires, in the absence of alkali, heating for several hours at 100°, in the presence of one equivalent of alcoholic potassium hydroxide gives in 30 min a 70% yield of the pure potassium salt of the oxyme (I).

The latter reaction can be represented as follows:



It is interesting to note the failure of our attempts to condense nitroacetic ester with phenylmercaptan or with aniline. In both cases, the starting materials were recovered unchanged, even when they were heated for a long time in the presence of alkali. Heating of a mixture of o-aminophenylmercaptan with α-nitropropionic ester led only to a small amount of o,o'-diaminodiphenyldisulfide. We also failed to cyclize either o-phenylenediamine, or o-aminophenyl with nitroacetic ester under analogous conditions. All these observations point out to the particular stability of the oxime of diketodihydrobenzo-1,4-thiazine. Isonitrosoacetic ester condenses with o-aminophenylmercaptan easily, giving the amide of benzothiazole-2-carboxylic acid. This amide is formed by the isomerization of the monoimide of 2,3-diketodihydrobenzo-1,4-thiazine, which is the initial product of this reaction.



EXPERIMENTAL*

2-Oxime of 2,3-diketodihydrobenzo-1,4-thiazine (I) [1]. A mixture of 5 g of o-aminothiophenol and 5.3 g of the ethyl ester of nitroacetic acid was heated at 100° for 4 hr. A yellow crystalline mass was formed. The product was washed with alcohol on a filter, and dried. Yield, 5.76 g (74%), m.p. 267° (dec.). After recrystallization from aqueous pyridine (1 : 1) the m.p. rose to 273° (dec.).

Found %: N 14.25, 14.24; S 16.57, 16.43. $C_8H_6O_2N_2S$. Calculated %: N 14.43; S 16.49.

The same product was obtained from 2,2-dichloro-3-ketodihydrobenzo-1,4-thiazine [5] and hydroxylamine.

A mixture of 0.46 g of the dichloro derivative and 3 ml of alcohol was treated with a solution of 0.2 g of hydroxylamine in 7 ml of alcohol prepared by adding to the corresponding amount of hydroxylamine hydrochloride the calculated amount of potassium hydroxide. The mixture was heated to boiling, thereupon pale yellow crystals separated out. Yield, 0.31 g (79%), m.p. 270° (dec.) raising to 273° (dec.) after recrystallization from alcohol.

Preparation of the potassium salt: a) Half a gram of the oxime was dissolved with heating in a solution of 0.5 g of potassium hydroxide in a mixture of 5 ml of alcohol and 5 ml of water. Upon slow cooling, yellowish platelets of the potassium salt precipitated out. Yield 3.95 g (66%). This salt is insoluble in alcohol, and sparingly soluble in boiling water (3.14 g in 100 ml). b) A mixture of 2.5 g of o-aminothiophenol, 2.66 g of nitroacetic ester, and 1.12 g of potassium hydroxide in 7 ml of alcohol was refluxed for 30 min. After cooling, the yellow precipitate formed was filtered off, and washed with alcohol and ether. Yield of the potassium salt, 3.27 g (70%).

Found %: S 13.84, 13.94; K 16.85, 16.81. $C_8H_5O_2N_2SK$. Calculated %: S 13.79; K 16.81.

Methyl ether of the 2-oxime of 2,3-diketodihydrobenzo-1,4-thiazine (II, R = CH_3). a) Four grams of the potassium salt of the oxime (I), and 11 g of dimethyl sulfate in 50 ml of xylene was heated with stirring for 6 hr at 120°. After cooling, the precipitate formed was filtered off and washed with hot water. Yield, 2.82 g (79%), m.p. 251° (from alcohol).

b) 2,3-Dichloro-3-ketodihydrobenzo-1,4-thiazine [5] (0.23 g) in 2 ml of alcohol was mixed with a solution of 0.14 g of the methyl ether of hydroxylamine in 2 ml of alcohol, and the mixture was heated to boiling. After cooling, the precipitate formed was filtered off, and washed with ether. Yield, 0.19 g (86%), m.p. 251° (from

*Melting points are corrected.

alcohol). This product did not give a melting point depression when mixed with the substance prepared as described under (a).

Found %: N 13.38, 13.44; S 15.40, 15.51. $C_9H_8O_2N_2S$. Calculated %: N 13.46; S 15.38.

Acetate of the 2-oxime of 2,3-diketodihydrobenzo-1,4-thiazine (II, R = $COCH_3$). Half a gram of the oxime (I) was dissolved in 10 ml of boiling acetic anhydride, and the mixture was refluxed for 2 hr. The crystals formed were filtered off, and washed with alcohol and ether. Yield, 0.56 g (93%); after being recrystallized twice from acetic anhydride the product melted at 218° (dec.).

Found %: N 11.82, 11.81; S 13.59, 13.64. $C_{10}H_8O_3N_2S$. Calculated %: N 11.86; S 13.56.

Benzoate of the 2-oxime of 2,3-diketodihydrobenzo-1,4-thiazine (II, R = COC_6H_5). A mixture of 1 g of the oxime (I), 0.8 g of benzoyl chloride, and 2 ml of pyridine was boiled for 5 min. After washing with water and alcohol, the crystalline product obtained weighed 1.43 g (93%); after recrystallization from acetone its m.p. was 235° (dec.).

Found %: N 9.45, 9.27. $C_{15}H_{10}O_3N_2S$. Calculated %: N 9.40.

2-Oxime of 2,3-diketo-4-methyldihydrobenzo-1,4-thiazine (III). A mixture of 2 g of nitroacetic ester and 2.1 g of N-methyl-o-aminothiophenol was heated for 2 hr at 100°. The precipitate formed was filtered off and washed with alcohol. Yield, 1.76 g (54%); m.p. after two recrystallizations from alcohol, 250°.

Found %: N 13.25; S 15.55, 15.56. $C_9H_8O_2N_2S$. Calculated %: N 13.46; S 15.38.

Acetate of the 2-oxime of 2,3-diketo-4-methyldihydrobenzo-1,4-thiazine. One gram of the oxime (III) was boiled for 1 hr with 3 ml of acetic anhydride and 1.3 g of anhydrous sodium acetate. Yield, 1.02 g (85%), m.p. 192° (from alcohol).

Found %: N 11.25, 11.31. $C_{11}H_{10}O_3N_2S$. Calculated %: N 11.20.

Benzoate of the 2-oxime of 2,3-diketo-4-methyldihydrobenzo-1,4-thiazine. It was prepared from the oxime (III) by the method described for the preparation of the benzoate of the oxime (I). Yield, 90%, m.p. 212° (from pyridine).

Found %: N 9.23, 9.06. $C_{16}H_{12}O_3N_2S$. Calculated %: N 8.97.

Methyl ether of the 2-oxime of 2,3-diketo-4-methyldihydrobenzo-1,4-thiazine (IV). a) The oxime (III) (2.5 g) was heated for 30 min with 30 ml of 20% sodium hydroxide solution. After cooling, the precipitated sodium salt was filtered off, and washed with alcohol and ether. It was then heated with stirring for 2.5 hr at 100° with 5 g of dimethyl sulfate in 20 ml of toluene. The precipitate formed was filtered off and washed with water. After recrystallization from petroleum ether, the yield was 0.72 g (27%), m.p. 131°.

b) The methyl ether of the oxime (I) (0.5 g) was boiled for 30 min with 10 ml of 20% sodium hydroxide solution. The sodium salt, which separated out, was filtered off and washed with alcohol and ether; then it was heated with an excess of methyl iodide in a sealed tube for 10 hr at 100°. Methyl iodide was removed by distillation and the solid residue was extracted with ligroin; evaporation of ligroin gave a colorless crystalline product, m.p. 131°.

This product did not depress the melting point of the substance prepared by method (a).

Found %: N 12.21, 12.20. $C_{10}H_{10}O_2N_2S$. Calculated %: N 12.60.

2-Acetylamino-3-keto-4-methyldihydrobenzo-1,4-thiazine (V). a) Two tenths of a gram of the oxime (III) was dissolved in 2 ml of concentrated hydrochloric acid; the solution was treated with 0.3 g of porous tin, and refluxed for about 40 min until the yellow color of the solution had disappeared. The solution was diluted with 50 ml of water, and tin was precipitated by hydrogen sulfide. The filtrate from tin sulfide was neutralized with sodium carbonate, and the yellow oil, which separated out, was extracted with ether. Distillation of ether (vacuum distillation at the end) gave 0.09 g (47%) of the oily amine, which was converted into its acetyl derivative, m.p. 159° (from water) by heating with acetic anhydride.

b) A solution of 1.8 g of 3-keto-4-methyldihydrobenzo-1,4-thiazine [6] in 3 ml of benzene was gradually, while boiling, treated with 1.35 g of sulfuryl chloride. The mixture was cooled, and the precipitate formed was filtered off and washed with a small volume of benzene, 1.41 g (66%) of 2-chloro-3-keto-4-methyldihydrobenzo-1,4-thiazine, m.p. 98-99° (from petroleum ether) being obtained.

Found %: N 6.40, 6.26; Cl 16.42, 16.51. C_9H_8ONSCl. Calculated %: N 6.55; Cl 16.26.

Half a gram of the monohalogen derivative and 4 ml of an alcoholic solution of ammonia was heated in a sealed tube on a water bath for 20 min; the alcohol was driven off, and the oil thus obtained was washed with water and dried in vacuum. Yield of the amine, 0.41 g (89%). After crystallization from water, the acetyl derivative of this substance melted at 159°, and did not depress the melting point of the substance prepared as described under (a).

Found %: N 11.70; S 13.90. $C_{11}H_{12}O_2N_2S$. Calculated %: N 11.86; S 13.56.

Amide of benzothiazole-2-carboxylic acid. A mixture of 2.5 g of o-aminothiophenol and 2.4 g of the ethyl ester of isonitrosoacetic acid was heated for 2 hr at 100°. The precipitated amide was filtered off and washed with ether. Yield, 1.22 g (34%), m.p. 224° (from alcohol) [5].

Found %: S 17.92, 17.91. $C_8H_6ON_2S$. Calculated %: S 17.97.

SUMMARY

Condensation of nitroacetic ester with o-aminophenylmercaptan gives the 2-oxime of 2,3-diketodihydrobenzo-1,4-thiazine. An analogous condensation with N-methyl-o-aminothiophenol leads to the 2-oxime of 2,3-diketo-4-methyldihydrobenzo-1,4-thiazine. The methylation, acetylation, and benzoylation products of the mentioned derivatives of benzo-1,4-thiazine were prepared and described.

Heating isonitrosoacetic ester with o-aminophenylmercaptan gives the amide of benzothiazole-2-carboxylic acid.

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STUDIES IN THE FURAN SERIES

XII. FURAN-2,5-DIALDEHYDE AND ITS REACTIONS WITH MALONIC ACID DERIVATIVES

K. Yu. Novitskii, V. P. Volkov, and Yu. K. Yur'ev

Moscow State University

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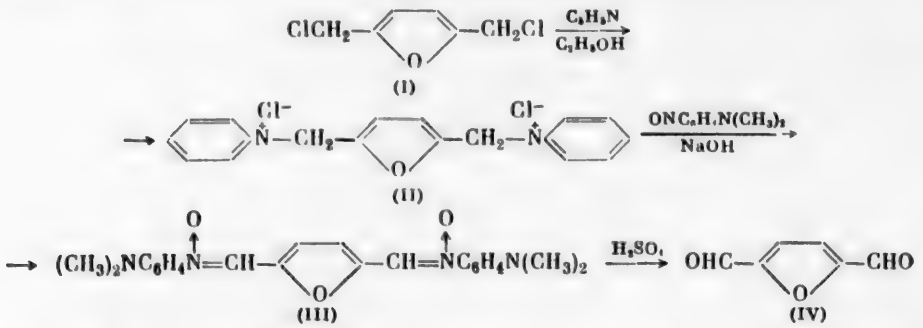
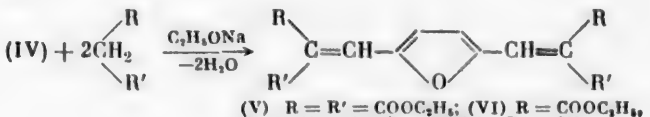
Furan-2,5-dialdehyde, obtained together with 5-formylpyromucic acid (total yield, 25-30%) by Cooper and Nuttall [1] by oxidation of 5-chloromethylfurfural with nitric acid was isolated by fractional crystallization. Later, these authors made this dialdehyde react with malonic acid and its ester [2]; however, nothing new has been reported on the reactions of this interesting compound, probably on account of the difficulty of its preparation.

In the present work we synthesized furan-2,5-dialdehyde from 2,5-bis (chloromethyl)-furan (I) which we prepared with a 48% yield by modifying the method described in the literature [3]. However, we failed to obtain the dialdehyde form of the complex compound of 2,5-bis(chloromethyl)-furan with urotropine. Then, we prepared the dipyridinium salt of 2,5-bis(chloromethyl)-furan (II), and converted it by the action of p-nitrosodimethylaniline into the substituted bis-nitronefuran-2,5-dialdehyde (III). Hydrolysis of the latter with diluted sulfuric acid led to furan-2,5-dialdehyde (IV) with a 79% yield, with respect to the 2,5-bis(chloromethyl)-furan used.*



While studying the condensations of furan-2,5-dialdehyde (IV) with malonic acid derivatives (malonic ester, ethyl ester and amide of cyanoacetic acid, and malonic acid dinitrile), we observed that these condensations occured very smoothly in the presence of catalytic amounts of sodium ethoxide, and that the reaction products were obtained with high yields (86-91%).



(V) R = R′ = $COOC_2H_5$; (VI) R = $COOC_2H_5$, R′ = CN; (VII) R = $CONH_2$, R′ = CN; (VIII) R = R′ = CN.

Hydrogenation of 2,5-bis(β,β-dicarbethoxyvinyl)-furan (V) in the presence of palladium, followed by hydrolysis of the ester of the tetracarboxylic acid, and decarboxylation of the acid, led to the formation of furan-2,5-dipropionic acid (IX). The same acid was also prepared by us from 2,5-bis(chloromethyl)-furan and the sodium

*For the preparation of aromatic aldehydes from primary halides by the action of p-nitrosodimethylaniline, see [4].

derivative of malonic ester. The two products were identical, and their constants coincided with those of the products obtained by reduction of furan-2,5-diacrylic acid [2], oxidation of furan-2,5-dipropionic aldehyde [5], or cyclization of dilevulinic acid [6].

EXPERIMENTAL

2,5-Bis(chloromethyl)-furan (I). Freshly distilled furfuryl alcohol (98 g) was placed in a four-necked 1 liter flask fitted with a stirrer, a dropping funnel, a thermometer, and a calcium chloride tube. Anhydrous pyridine (95 g) was added while stirring, followed by 200 ml of absolute chloroform. The mixture was cooled to −10°, and treated dropwise, with efficient stirring, while maintaining the temperature between −10° and 0°, with a solution of 131 g of freshly distilled thionyl chloride in 50 ml of absolute chloroform. Addition took 1 hr; then the reaction mixture was immediately poured in ice-cold water (200 ml). The lower oily layer was separated out, and washed, in succession, with 100 ml of ice-cold water, and two portions of 5% sodium hydroxide solution cooled to 0° (during these operations, ice shavings must be added to the water and to the sodium hydroxide solution). Finally, the product was dried with anhydrous potassium carbonate at 0°. The furfuryl chloride thus obtained was not submitted to further purification, and was chloromethylated as such, in chloroform solution.

The flask used in the preceding preparation was fitted with a reflux condenser and with two tubes for the introduction of gas. Absolute chloroform (250 ml), 27.0 g of dry paraform, and 8 g of anhydrous zinc chloride were placed in the flask, and the mixture was saturated with dry hydrogen chloride. Then, while stirring and passing nitrogen gas and a weak current of hydrogen chloride through the mixture, the solution of furfuryl chloride prepared as indicated above was added dropwise over a period of 1.5-2 hr. The temperature of the reaction mixture rose to 35° during the addition. Hydrogen chloride was passed through the reaction mixture for 1 hr more at this temperature, and then for 2 hr at 40-45° (bath temperature). The cooled mixture was poured into 200 ml of ice-cold water. After filtration through glass wool, the chloroform layer was washed with ice-cold water, and dried with anhydrous potassium carbonate at 0°. Removal of the solvent and distillation of the reaction product was carried out under reduced pressure in a stream of nitrogen. Yield 78.8 g (48%) of the bis(chloromethyl) derivative.

B.p. 93-95° (10 mm), m.p. 27-28° (from a mixture of ether and petroleum ether). Reported: b. p. 92-99° (14 mm), m.p. 27° [3].

Furan-2,5-dialdehyde (IV). A solution of compound (I) (8.25 g) in 10 ml of alcohol, and 11.9 g of pyridine were introduced into a flask fitted with a reflux condenser. The mixture was heated for 1 hr on a boiling water bath: This resulted in the formation of crystals of the dipyridinium salt (II). The mixture was cooled, the crystals rapidly filtered off, washed with acetone and absolute ether, and dried in vacuum over calcium chloride. The mother liquor yielded a further amount of the salt (II). Yield of (II), 14.9 g (92%). Salt (II) appears as colorless hygroscopic crystals, readily soluble in water and methanol, moderately soluble in ethanol, and sparingly soluble in ether and acetone.

M.p. 130-132° (from a mixture of dry acetone and absolute alcohol).

Found %: Cl 21.55, 21.62. $C_{16}H_{16}ON_2Cl_2$. Calculated %: Cl 21.94.

A solution of 15 g of p-nitrosodimethylaniline in 350 ml of alcohol was treated with a solution of 14.9 g of the salt (II) in 25 ml of water (it is not necessary to isolate the salt (II): Its alcoholic solution prepared as described above can be used as such). To the solution thus obtained was added rapidly (5 min) with stirring and keeping the temperature at −4°, 100 ml of 1 N sodium hydroxide solution cooled to 0° (the reaction mixture became red). The product was allowed to stand for 10-12 hr at 0°; thereupon, a red microcrystalline precipitate separated out. Water (250 ml) was added, the mixture was allowed to stand for a further 1 hr at 0°. The precipitate was filtered off, washed with cold dilute alcohol, and dried in vacuum over calcium chloride. Yield of furan-2,5-bis(N-p-dimethylaminophenylnitrone) (III), 17.8 g (91% w.r. to substance (I)]; m.p. 226-227° (from alcohol). (III) appears as red crystals readily soluble in acetone and chloroform, and moderately soluble in benzene and carbon tetrachloride.

Found %: C 67.24, 67.41; H 6.32, 6.37. $C_{22}H_{24}O_3N_4$. Calculated %: C 67.33; H 6.17.

Substance (III) (17.8 g) was carefully dissolved in 200 ml of 2 N sulfuric acid at 0°; the dark red solution was left to stand for 30 min at 25°. Then, it was extracted with four 200 ml portions of ether. The sulfuric acid solution was left to stand for a further 30 min at 40-50° to ensure complete hydrolysis of substance (III), and was extracted once more with 200 ml of ether after cooling to 25°. The combined ethereal extracts were washed with

water, sodium carbonate solution, water, and finally dried over anhydrous magnesium sulfate. After removal of ether by distillation, 4.9 g of furan-2,5-dialdehyde (IV), m.p. 105-106° was obtained. After recrystallization from carbon tetrachloride, the m.p. of (IV) rose to 109-110°, in agreement with the reported data [1]. (IV) appears as pale yellow crystals readily soluble in chloroform, hot water, and hot alcohol, moderately soluble in carbon tetrachloride, ether, acetone, and benzene, and sparingly soluble in petroleum ether.

Found %: C 58.21, 58.39; H 3.59; 3.59. $C_6H_4O_3$. Calculated %: C 58.07; H 3.25.

The diphenylhydrazone of (IV) melted at 206-207° (from toluene), reported m.p. 206-207° [1].

The reactions of furan-2,5-dialdehyde (IV) with malonic acid derivatives were carried out as described for malonic ester.

a) 2,5-Bis(β,β-dicarbethoxyvinyl)-furan (V). A solution of 1.24 g of the dialdehyde (IV) in the minimum volume of anhydrous alcohol (20 ml) was mixed with 3.2 g of malonic ester. After addition of 4-5 drops of a 5% alcoholic solution of sodium ethoxide, the mixture was left to stand for 30 min at 20° and for 1-2 hr at 0°. The crystals which separated out were filtered off, washed with cold alcohol, and dried in vacuum at 50°. Yield of ester (V), 3.5 g (80%). (V) appears as yellowish crystals, m.p. 89-90° (from alcohol), reported m.p. 90-91° [2].

b) 2,5-Bis(β-carbethoxy-β-cyanovinyl)-furan (VI). The carbethoxynitrile (VI) was prepared from 1.24 g of the dialdehyde (IV) and 2.26 g of cyanoacetic ester. Yield, 2.25 g (87%). (VI) appears as yellow crystals, m.p. 155-155.5° (from alcohol).

Found %: C 60.85, 61.00; H 4.59, 4.60. $C_{16}H_{14}O_5N_2$. Calculated %: C 61.14; H 4.49.

c) 2,5-Bis(α-cyano-β-acrylamide)-furan (VII). Substance (VII) was prepared from 1.24 g of the dialdehyde (IV), and 1.68 g of cyanoacetic acid amide. Yield, 2.2 g (80%). (VII) appears as yellow crystals, m.p. 297-298° (from glacial acetic acid).

Found %: C 56.41, 56.45; H 3.40, 3.51. $C_{12}H_8O_3N_4$. Calculated %: C 56.25; H 3.15.

d) 2,5-Bis(β,β-dicyanovinyl)-furan (VIII). The dinitrile (VIII) was prepared from 1.24 g of the dialdehyde (IV) and 1.32 g of malonic acid dinitrile. Yield, 2.0 g (91%). (VIII) appears as pale brown crystals, m.p. 207-208° (from alcohol).

Found %: C 65.86, 65.92; H 1.92, 1.98. $C_{12}H_4ON_4$. Calculated %: C 65.45; H 1.83.

Furan-2,5-dipropionic acid (IX). a) A solution of 0.82 g of 2,5-bis(β,β-dicarbethoxyvinyl)-furan (V) in 10 ml of absolute acetone was hydrogenated in the cold with shaking in the presence of palladium (5%) on barium sulfate. In the course of 12 hr, 98% of the theoretical amount of hydrogen was absorbed. The catalyst was separated out and washed with acetone. After removal of the solvent by distillation in vacuum, the yellow oil (0.8 g) was mixed with a solution of 0.45 g of potassium hydroxide in 0.6 ml of water, and refluxed for 2 hr. Then, the reaction product was cooled and extracted with ether. The aqueous solution of the potassium salt of the acid (IX) was cooled to 0°, acidified with 2 N sulfuric acid, and extracted with ether. The ethereal extract was dried with anhydrous magnesium sulfate. The residue remaining after ether was distilled off crystallized out completely. Yield of the acid (IX), 0.18 g (43%), m.p. 152-153° (from water); reported m.p. 151-152° [2], 153-154° [6], and 154-154.5° [5].

Found: Acid Equiv. 104.0, 105.0. $C_{10}H_{12}O_5$. Calculated: Acid Equiv. 106.1.

b) A solution of sodium ethoxide prepared from 1.15 g of sodium and 25 ml of anhydrous alcohol in a three-necked flask fitted with a reflux condenser, a stirrer, and a dropping funnel was treated slowly and dropwise, at 50° with 8 g of malonic ester. The clear solution thus obtained was treated dropwise, while cooling with ice-cold water, and over a period of 30 min, with a solution of 3.3 g of the bischloromethyl derivative (I) in 5 ml of anhydrous alcohol. Stirring was continued for 1 hr at 20°, and for 3-4 hr on a boiling water bath. Alcohol was driven off, and the residue treated with 10 ml of water. The oily layer so formed was separated out, and the aqueous layer was extracted with ether thrice. The ethereal extracts were dried over anhydrous magnesium sulfate; then ether and unchanged malonic ester were driven off in vacuum. The remaining product was dissolved in anhydrous benzene and chromatographed on alumina. Elution was carried out with absolute benzene. After the solvent was distilled off, the residual yellowish oil (2.75 g) was submitted to alkaline hydrolysis as described under(a). Yield of the acid, 0.55 g [13% w.r. to compound (I)], m.p. 152-153° (from water). This substance did not depress the melting point of the sample prepared by method (a).

SUMMARY

1. Hydrolysis of the bis-nitrone, which is easily prepared via the pyridinium salt from 2,5-bis(chloromethyl)-furan, leads to furan-2,5-dialdehyde with an over-all yield of 79%.

2. Furan-2,5-dialdehyde readily condenses with malonic acid derivatives. 2,5-Bis(β,β-dicarbethoxyvinyl)-furan, 2,5-bis(β-carbethoxy-β-cyanovinyl)-furan, 2,5-bis(α-cyano-β-acrylamide)-furan, and 2,5-bis(β,β-dicyanovinyl)-furan were prepared by this reaction.

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SYNTHETIC STUDIES IN THE FIELD OF VITAMINS OF GROUP B_6

I. SYNTHESIS OF 2-METHYL-3-HYDROXY-4-METHOXYMETHYL-5-HYDROXYMETHYLPYRIDINE

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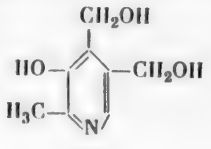
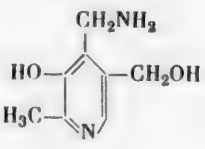
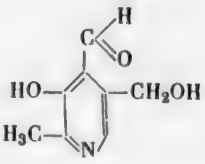
Original article submitted February 20, 1960

The group of vitamins B_6 is composed of three related substances: pyridoxine (I), pyridoxamine (II) and pyridoxal (III), which are interconvertible in the organism.


(I)

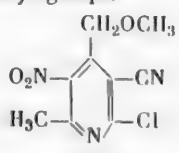

(II)


(III)

The latter (III) is the main representative of this group. Its phosphate ester (pyridoxal phosphate) is known in medical practice as the prosthetic group of the decarboxylase which splits glutamic acid to β-aminobutyric acid and carbon dioxide. A peculiar character of glutamic acid decarboxylase in the living organism is its exclusive localization in the nervous system [1]. This points to the specific role of pyridoxal, pyridoxine, and pyridoxamine in the activity of the nervous cells.

Of the greatest interest in the preparation scheme of the vitamins of the B_6 group is the synthesis of 2-methyl-3-hydroxy-4-methoxymethyl-5-hydroxymethyl pyridine (VI). Several methods have been proposed for the synthesis of this important intermediate [2]. However, the methods proposed for the conversion of (IV) into (VI) do not lead to useful results because of experimental difficulties and low yields.

We studied a method for the preparation of 2-methyl-3-hydroxy-4-methoxymethyl-5-hydroxymethylpyridine (VI) based upon the reduction of 3-nitro-4-methoxymethyl-5-cyano-6-chloropyridine (IV) to 2-methyl-3-amino-4-methoxymethyl-5-aminomethylpyridine (V) followed by the replacement of the amino groups of the latter compound (V) with hydroxyl groups.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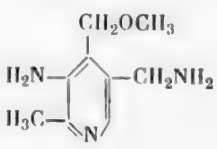
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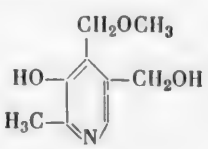
(VI)

The starting material for the synthesis of 2-methyl-3-nitro-4-methoxymethyl-5-cyano-6-chloropyridine (IV) was 2-methyl-3-nitro-4-methoxymethyl-5-cyano-6-hydroxypyridine.

We elaborated a method for the simultaneous elimination of chlorine, and reduction of the nitro and cyano groups to obtain product (V). The earlier methods designed to achieve the gradual reduction of the functional groups of compound (IV) [2], and also to convert (IV) into (V) in one stage by the use of various catalysts [3, 4] were time-consuming and proceeded with low yields.

We studied several modifications of the reaction. Catalytic reduction with palladium on charcoal prepared after Gatterman [5] led to a 90% yield when the duration of the hydrogenation was 6.5 hr. Reduction with the same catalyst prepared according to Zelinskii [6] required 5.5 hr, and the yield was 71.3%. Under conditions of low temperature, and using 2.32% of palladium with respect to the compound under investigation (IV), a 87-90% yield was achieved with hydrogenation for 2-3 hr [3].

We obtained the best results when we used in the catalytic reduction 1.5% palladium with 12% activated charcoal in dilute (1 : 18) hydrochloric acid. The reduction required 1 hr, and the yield was 94.3%.

A method is known for the replacement of the amino groups of (V) by hydroxyl groups by diazotization in a sulfuric acid medium [7]. We increased the yield of the hydrochloride of 2-methyl-3-hydroxy-4-methoxymethyl-5-hydroxymethylpyridine to 72.9% with respect to 2-methyl-3-nitro-4-methoxymethyl-5-cyano-6-chloropyridine by treating (V) with sodium nitrite in a heated aqueous solution of hydrochloric acid.

EXPERIMENTAL

2-Methyl-3-amino-4-methoxymethyl-5-aminomethylpyridine dihydrochloride (V). A solution of 0.06 g of palladium chloride in 2 ml of hydrochloric acid (d^{20}_4 1.18) was mixed with 25 ml of distilled water and 0.24 g of activated charcoal, and reduced for 20 min. Then, 2 g of 2-methyl-3-nitro-4-methoxymethyl-5-cyano-6-chloropyridine in 25 ml of water was added to the mixture, and reduction was resumed. The volume of hydrogen absorbed in 40 min was 1150 ml (theoretical amount, 1100 ml). The catalyst was separated and washed with 5 ml of boiling alcohol. After alcohol was driven off, 0.03 g of the starting material, m.p. 72-73° was recovered. The filtrate was evaporated, and the residue crystallized from 150 ml of absolute alcohol. Yield, 1.98 g (94.3%), m.p. 230-231°.

Found %: C 42.45; H 6.73; N 16.53. $C_9H_{15}ON_3 \cdot 2HCl$. Calculated %: C 42.53; H 6.74; N 16.54.

The dipicrate of 2-methyl-3-amino-4-methoxymethyl-5-aminomethylpyridine melted at 214-215° (from alcohol).

Found %: C 39.64; H 3.23; N 19.71. $C_9H_{15}ON_3 \cdot 2C_6H_3O_7N_3$. Calculated %: C 39.44; H 3.31; N 19.71.

2-Methyl-3-hydroxy-4-methoxymethyl-5-hydroxymethylpyridine hydrochloride (VI). a) A solution of 1.25 g of 2-methyl-3-amino-4-methoxymethyl-5-aminomethylpyridine dihydrochloride (m.p. 230-231°) in a mixture of 32 ml of distilled water and 1.7 ml of hydrochloric acid (d^{20}_4 1.18) heated to 80° was treated during 1.5 hr with 0.75 g of sodium nitrite dissolved in 3 ml of water. After stirring for a further period of 30 min at 80° (test with starch-iodide paper), the solution was evaporated to dryness in vacuum (10 mm), and the residue was treated with 30 ml of absolute alcohol. The yield of substance (VI) thus produced was 0.79 g (73.1%), m.p. 173-174°.

Found %: C 49.23, 49.16; H 6.40; N 6.44. $C_9H_{13}O_3N \cdot HCl$. Calculated %: C 49.20; H 6.42; N 6.37.

b) Reduction of palladium chloride, and hydrogenation of 2 g of 2-methyl-3-nitro-4-methoxymethyl-5-cyano-6-chloropyridine was carried out as already described. The colorless solution obtained after separation of the catalyst was treated with 2.5 ml of hydrochloric acid. After heating to 80°, a solution of 1.22 g of sodium nitrite in 5 ml of water was added, and the reaction was completed as described above. Yield, 1.32 g (72.9%), m.p. 173-174°.

SUMMARY

1. A method is proposed for the simultaneous elimination of chlorine, and the reduction of the nitro and cyano groups in 2-methyl-3-nitro-4-methoxymethyl-5-cyano-6-chloropyridine.

2. 2-Methyl-3-hydroxy-4-methoxymethyl-5-aminomethylpyridine was synthesized.

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STUDY OF PYRAZOLES

XIV. DEHYDRATION WITH SULFUR OF PYRAZOLINES HAVING FUNCTIONAL SUBSTITUENTS IN THE PYRAZOLINE RING

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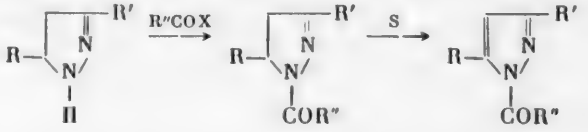
Original article submitted March 1, 1960

Pyrazoles having no substituent on the nitrogen atom can be converted into the corresponding N-acylpyrazoles by the action of acylating agents. However, when there are different substituents in positions 3 and 5 of the pyrazole ring, i.e., when the ring is unsymmetrical with respect to the two nitrogen atoms, a difficultly purifiable mixture of isomers is always formed [1].

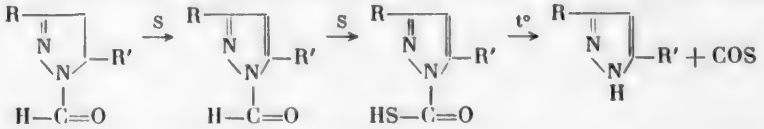
Previously [2, 3], by taking advantage of the absence of tautomerism in pyrazolines, we carried out their monoalkylation, and then, upon dehydrogenation, we obtained the N-substituted unsymmetrical pyrazoles. We decided to apply this method to the synthesis of unsymmetrical N-acylpyrazoles, according to the scheme:



With this aim, we carried out the dehydrogenation of N-formyl-, N-acetyl-, and N-benzoylpyrazolines with the help of sulfur. It appeared that the reaction did not proceed in the expected way. In all the cases dehydrogenation was accompanied by the removal of the acyl radical from the nitrogen atom. Thus, dehydrogenation of 1-formyl-4-ethyl-5-propyl-, 1-formyl-4-isopropyl-5-isobutyl-, and 1-formyl-5-phenylpyrazolines led only to the corresponding deacetylated pyrazoles with about 40% yields. Dehydrogenation of 1-acetyl-3,5-diphenylpyrazoline gave 3,5-diphenylpyrazole with a 84% yield. In the case of 1-benzoyl-5-phenylpyrazoline, dehydrogenation gave, together with 3(5)-phenylpyrazole, a small yield of benzoic acid.

To be used as a dehydrogenating agent in the case of N-acyl derivatives, sulfur has to be taken in amounts double of the calculated. If acylpyrazolines are heated with one equivalent of sulfur, instead of two, the yields of pyrazoles drop to 15-25%, and almost half of the acylpyrazoline is recovered unchanged.

We assume that N-formylpyrazolines are first dehydrogenated by sulfur to the corresponding N-formylpyrazoles, which react at the same with a second molecule of sulfur forming unstable N-thiocarbamic acids. The latter are easily converted upon heating to pyrazoles unsubstituted at the nitrogen atom, carbon oxysulfide being formed.



Obviously, oxidation of formylpyrazole by sulfur proceeds more easily and rapidly than dehydrogenation and oxidation of formylpyrazoline, and this fact determines the general trend of the process.

In order to confirm this mechanism, we studied the gases which are formed during the reaction. We succeeded in showing the presence of calbon oxysulfide in these gases. Probably, the situation is more complicated in the case of N-acetyl- and N-benzoylpyrazolines. Products resulting from a reaction at the acetyl group could not be detected at all; in the case of the benzoyl group we were able to isolate only an insignificant amount of benzoic acid.

Apparently, in this case, the hydrogen sulfide produced during the reaction hydrolytically breaks the already very much weakened amide linkage [4, 5] of acylpyrazole.

Under drastic conditions of the reaction, and in the presence of free sulfur and hydrogen sulfide, thioacids can undergo disproportionation with the formation of benzoic acid.

Pyrazolines, which have cyano, carbonyl, or carboxyl groups attached to the ring carbon atoms, do not undergo smooth dehydrogenation with sulfur. We failed to prepare the corresponding pyrazoles from 4-phenyl-3-cyanopyrazoline and 4-phenyl-3-acetylpyrazoline. These reactions proceeded with very strong resinification. The diethyl ester of pyrazoline-3,4-dicarboxylic acid gave, upon heating with sulfur, a good yield of the diethyl ester of cyclopropane-1,2-dicarboxylic acid.

EXPERIMENTAL

1-Formyl-5-phenylpyrazoline. A mixture of 26.8 g of 5-phenylpyrazoline (b.p. 136-138° (13 mm) [6]) and 30 ml of 85% formic acid was submitted to vacuum distillation. Excess of formic acid and water distill first, followed by 23.0 g (70%) of the formyl derivative b.p. 180-187° (8 mm). The latter appears as a thick oil which crystallizes out very slowly, m.p. 69-70° (from benzene).

Found %: N 15.90, 15.90. $C_{10}H_{10}ON_2$. Calculated %: N 16.06.

1-Acetyl-5-phenylpyrazoline. It was prepared in an analogous way by reaction with acetic anhydride. Yield, 74.2%, b.p. 180-182° (6 mm). It appears as a very thick slowly crystallizing oil, m.p. 53-54° (from benzene).

Found %: N 15.35, 15.30. $C_{11}H_{12}ON_2$. Calculated %: N 14.89.

1-Benzoyl-5-phenylpyrazoline. A mixture of 26.8 g of 5-phenylpyrazoline and 45.2 g of benzoic anhydride in 100 ml of dry benzene was refluxed for 1 hr. Then, the reaction mixture was shaken for 2 hr with 200 ml of 2 N sodium hydroxide solution. The benzene layer was separated out, washed with water, and dried over magnesium sulfate. The benzoylpyrazoline derivative crystallized out after evaporation of benzene. Yield, 38.5 (81%), m.p. 98-99° (from benzene).

Found %: N 11.65, 11.60. $C_{16}H_{14}ON_2$. Calculated %: N 11.85.

1-Acetyl-3,5-diphenylpyrazoline. A mixture of 44.4 g of 3,5-diphenylpyrazoline [6] and 28 ml of acetic anhydride was heated to boiling for 15 min. Addition of water to the reaction product led to the separation of 43.5 g (82%) of the acetyl derivative, m.p. 129-130° (from a mixture of benzene and petroleum ether).

Found %: N 11.10, 11.00. $C_{17}H_{16}ON_2$. Calculated %: N 10.69.

Dehydrogenation of 1-formyl-4-ethyl-5-propylpyrazoline. A mixture of 84 g of 1-formyl-4-ethyl-5-propylpyrazoline (b.p. 153-157° (36 mm) [7]) and 32 g of sulfur was refluxed until evolution of hydrogen sulfide ceased (about 16 hr). The reaction mixture was distilled in vacuum thrice giving 34.5 g (50%) of 4-ethyl-5-isopropylpyrazole, b.p. 137-141° (17 mm), $n^{20}D$ 1.4872, d^{20}_4 0.9397.

The picrate prepared from this substance melted at 133° (from 50% alcohol) [2] and did not depress the m.p. of an authentic sample of 4-ethyl-5-isopropylpyrazole picrate.

In order to elucidate the decomposition of the gases formed during the reaction (for this purpose the reaction was carried on with one tenth of the amounts used in the foregoing experiment), they were processed according to Avdeeva's method [8]. The effluent gases were passed through three wash bottles connected in series, and containing a concentrated iodine solution in aqueous potassium iodide in order to ensure the complete absorption of hydrogen sulfide. Then, carbon oxysulfide was absorbed in an aqueous alcoholic solution of potassium hydroxide (1 g of potasdium hydroxide in 2 g of alcohol and 1 g of water). The presence of carbon oxysulfide in the gases having passed through iodine solution was proved by the fact that acidification of the alkaline solution in the last wash bottle led to the separation of a mixture of carbon oxysulfide and hydrogen sulfide. Moreover, the gas which has passed through iodine solution had a characteristic smell; when this gas was absorbed in water after a passage through alkali solution, the aqueous solution developed a hydrogen sulfide smell upon standing for a few hours (hydrolysis).

Dehydrogenation of 1-formyl-4-isopropyl-5-isobutylpyrazoline. It was carried out as described for the dehydrogenationof 1-formyl-4-ethyl-5-propylpyrazoline. Forty-nine grams of 1-formyl-4-isopropyl-5-isobutylpyrazoline

(b.p. 132-136° (9 mm) [7]) and 16 g of sulfur gave after three distillations 14.2 g (34%) of 4-isopropyl-5-isobutylpyrazole, b.p. 144-148° (13 mm), $n^{20}D$ 1.4800, d^{20}_4 0.9064.

The picrate prepared from this substance melted at 71° (from 50% alcohol) [2], and did not depress the m.p. of an authentic sample of 4-isopropyl-5-isobutylpyrazole picrate.

Dehydrogenation of 1-formyl-5-phenylpyrazoline. A mixture of 17.4 g of 1-formyl-5-phenylpyrazoline and 6.4 g of sulfur was heated in a small Claisen flask until evolution of hydrogen sulfide ceased completely (180-230°, 1.5 hr); the reaction mass was distilled in vacuum giving 7.6 g (53%) of 3(5)-phenylpyrazole, b.p. 200-204° (20 mm), m.p. 76° (from petroleum ether) [2], no m.p. depression when mixed with an authentic sample of this compound.

Dehydrogenation of 1-acetyl-3,5-diphenylpyrazoline. It was carried out in an analogous way: 26.4 g of 1-acetyl-3,5-diphenylpyrazoline and 6.4 g of sulfur led to a 84% yield of 3,5-diphenylpyrazole, b.p. 317° (160 mm), m.p. 204° (from methanol) [2], giving no m.p. depression when mixed with an authentic sample of this compound

Dehydrogenation of 1-benzoyl-5-phenylpyrazoline. A mixture of 24.8 g of benzoyl-5-phenylpyrazoline and 3.2 g of sulfur was heated in a small Claisen flask until evolution of hydrogen sulfide ceased. Vacuum distillation of the reaction mass led to two fractions: a) a low-boiling product (2.1 g) b.p. 130-150° (5 mm), which rapidly crystallized out upon standing in the refrigerator. This product gave 1.6 g of pure benzoic acid, m.p. 119-120° (from water) upon purification, giving no m.p. depression when mixed with an authentic sample of benzoic acid. b) a high-boiling oil (12.8 g), b.p. 177-189° (5 mm), purification of which led to 6.9 g (51.5%) of pure 3(5)-phenylpyrazole, m.p. 78-80° (from petroleum ether). This substance did not give a m.p. depression when mixed with an authentic sample of 3(5)-phenylpyrazole.

Diethyl ester of pyrazoline-3,4-dicarboxylic ester. An ethereal solution of 5.2 g of diazomethane was treated at room temperature with 22 g of diethylfumarate. A rapid decoloration of the reaction mixture was observed. After standing for 3 hr, the mixture gave 26.5 g (98%) of the diethyl ester of pyrazoline-3,4-dicarboxylic acid, appearing as colorless crystals, m.p. 87-88° (from ether).

Found %: N 13.30, 13.12. $C_9H_{14}O_4N_2$. Calculated %: N 13.08.

Dehydrogenation of the diethyl ester of pyrazoline-3,4-dicarboxylic acid. A mixture of 10 g of the diethyl ester of pyrazoline dicarboxylic acid and 1.3 g of sulfur was gradually heated; evolution of nitrogen started at 150-180°; it was followed by a small amount of hydrogen sulfide. The residue was distilled in vacuum twice giving 5.7 g (60%) of the diethyl ester of cyclopropane-1,2-dicarboxylic acid, b.p. 107-108° (11 mm), d^{20}_4 1.0570 [9].

Dehydrogenation of 3-cyano-4-phenylpyrazoline. A mixture of 17.2 g of 3-cyano-4-phenylpyrazoline [10] and 3.2 g of sulfur was heated on a sand bath. The reaction mass resinified at 180-200°, and evolution of hydrogen sulfide was very sluggish. The reaction product did not yield any well-characterized substance upon purification.

Dehydrogenation of 3-acetyl-4-phenylpyrazoline. A mixture of 18.8 g of 3-acetyl-4-phenylpyrazoline (m.p. 101° [11]) and 3.2 g of sulfur was heated on a sand bath. At 170-195°, resinification occurred. It was not possible to isolate any definite compound from this reaction product.

SUMMARY

1. N-Formyl-, N-acetyl- and N-benzoylpyrazolines are dehydrogenated by sulfur to the corresponding pyrazoles having no substituents on the heterocyclic nitrogen atoms.

2. A mechanism is proposed for the dehydrogenation of formylpyrazolines with sulfur.

3. Pyrazolines having cyano-, carbethoxy- or carbonyl groups attached to the ring carbon atoms do not undergo dehydrogenation to the corresponding pyrazoles by the action of sulfur.

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STUDY OF PYRAZOLES

XV. REACTIONS OF PYRAZOLES WITH HALOGEN COMPOUNDS OF SULFUR

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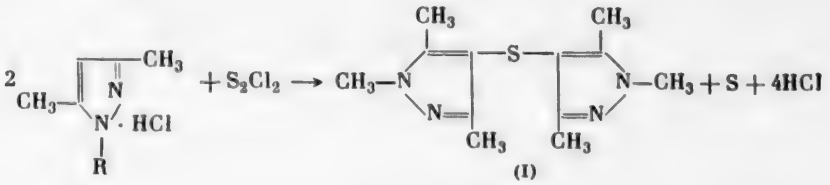
Pyrazoles with a sulfur atom in position 4 of the ring are almost unknown; they are interesting as potential pharmacological agents. We decided to take advantage of the superaromatic properties of the pyrazole ring (i.e., the extreme mobility of the hydrogen atom in position 4 of the ring toward electrophilic substituents), which are displayed in several reactions (halogenation, phosphorylation, benzylation, benzoylation, etc.), to introduce a sulfur atom directly in the pyrazole ring by the action of halogen compounds of sulfur.

However, sulfur monochloride reacted with 1,3,5-trimethylpyrazole so vigorously, that the greater part of the products resinified, and we were able to isolate the sulfide (I) with only a 25-35% yield. By depressing the activity of the ring through salt formation (hydrochloride), we succeeded to run this reaction very smoothly at 80-110°, a high yield being produced.

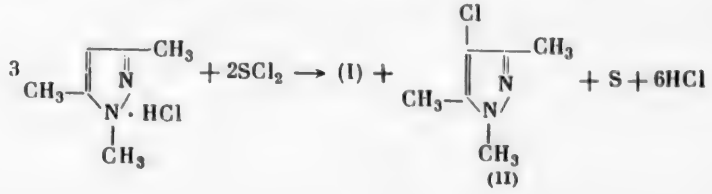


Other 1-alkyl substituted pyrazoles reacted in exactly the same way, although it should be noted that some difficulties were met with during the identification of the sulfides obtained in these reactions. These sulfides are high boiling uncrystallizable oils which decompose somewhat upon distillation. Their hydrochlorides and picrolonates do not crystallize out, and the only characteristic solid derivatives are the picrates which must be crystallized from absolute ether.

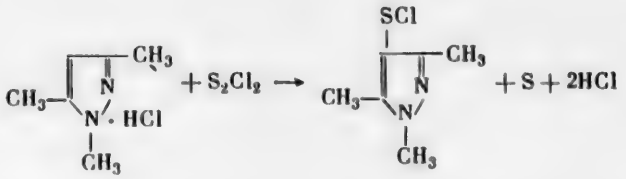
The formation of sulfides upon the action of sulfur monochloride, with the simultaneous appearance of sulfur, instead of the formation of a disulfide bridge $-S-S-$, has already been reported by Boeseken [1]; however, this author has carried out the reactions in the presence of anhydrous aluminum chloride.

The reaction proceeds in an analogous way in the case of 1-arylpyrazoles, although it is less vigorous, and the yields are somewhat lower, but still fully satisfactory.

The use of sulfur dichloride also leads to the formation of the sulfide (I). However, because of the reaction $2SCl_2 \rightarrow S_2Cl_2 + Cl_2$, 1,3,5-trimethyl-4-chloropyrazole (II) is also formed.

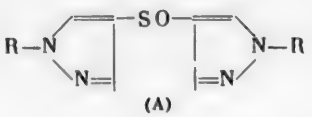


By carrying out the reaction between sulfur monochloride and 1,3,5-trimethylpyrazole in such a way as to have sulfur monochloride in excess during the whole duration of the experiment, we succeeded to avoid bridging between the pyrazole rings, and to obtain a chlorosulfide.



The chlorosulfide derivative appeared as crystals with a low melting point, boiling at a relatively low temperature, and easily forming a low-melting picrate. This compound was readily soluble in acids, and it was only slightly decomposed when treated with hot alkalies for 15-30 min. We did not investigate it with more detail, as not only the chlorosulfide derivative, but even its picrate were rather strongly lacrymatory substances.

The action of thionyl chloride on pyrazoles gave rather interesting results. In this case we could have expected the formation of the sulfoxide (A), as this reaction in the presence of anhydrous aluminum chloride constitutes the synthetic method for the preparation of sulfoxides in the aromatic series.



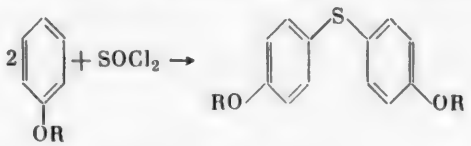
(A)

It appeared that 1-alkylpyrazoles reacted with thionyl chloride rather vigorously. However, when we lowered the reactivity of 1,3,5-trimethylpyrazole by converting it into its hydrochloride, we succeeded to obtain a yield of about 40% of the same sulfide (I) as in the case of sulfur monochloride. Together with the sulfide (I), we obtained a considerable amount of 1,3,5-trimethyl-4-chloropyrazole (II).

$$2PyrSOPyr \longrightarrow PyrSPyr + PyrSO_2Pyr$$

Our first assumption, viz., that the sulfide could have been formed by the disproportionation of the sulfoxide, was not confirmed, as all our efforts to isolate the corresponding sulfone did not give the contemplated result.

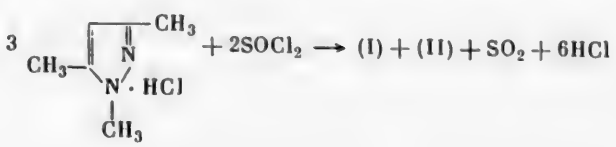
Analogous cases are those of anisole and phenetole [2], the authors explaining the reaction:



by the decomposition of thionyl chloride according to the scheme:

$$2SOCl_2 \longrightarrow SCl_2 + SO_2 + Cl_2$$

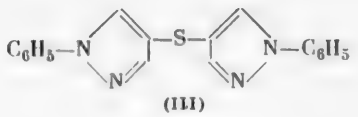
In our case the role of chlorine-binding agent is assumed by pyrazole which readily undergoes chlorination. The reaction is accompanied by a rather strong evolution of hydrogen chloride and sulfur dioxide.



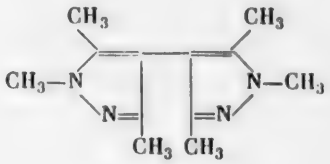
The identity of the sulfides obtained in the reactions with sulfur monochloride and thionyl chloride was ascertained by mixed melting point determinations carried out on the sulfides themselves, and their espective picrates and sulfones. The sulfides were oxidized to the corresponding sulfones with the calculated amounts of neutral potassium permanganate, or by prolonged boiling with peracetic acid. Treatment with cold peracetic acid (leading in the aromatic series to sulfoxides [3]) did not affect divalent sulfur in our case. This may be explained by the presence of methyl groups in positions 3 and 5 (spatial restrictions). When the present work has ready for publication, it was reported [4] that the action of thionyl chloride on 1-phenylpyrazole was observed during an investigation of the formylation of pyrazoles. The authors of this paper described the reaction product as a sulfoxide; however, its melting point was practically the same as that of the sulfide (III) we obtained by treating 1-phenylpyrazole with sulfur. After repeating the experiments of these authors and checking their results, we came to the conclusion that they have really mistaken the sulfide formed in the reaction for the sulfoxide.

Sulfides prepared by different procedures, as well as the sulfones prepared from these sulfides did not give depressions of mixed melting points.

All attempts to prepare the sulfoxide from 1-phenylpyrazole with the help of anhydrous aluminum chloride under different conditions gave negative results; in all cases, the starting pyrazole was recovered. We also failed to obtain the sulfoxide from 1,3,5-trimethylpyrazole by treating it with $SOCl_2$ in the presence of aluminum chloride. Under mild conditions of the reaction, the starting pyrazole was recovered, while under more drastic conditions a condensation product was obtained which did not contain sulfur, and whose analytical results corresponded to those calculated for bis-1,3,5-trimethylpyrazolyl-4 (IV). However, the formation of compound (IV) in this reaction appears to be improbable.



(III)



(IV)

EXPERIMENTAL

1,3,5-Trimethylpyrazolyl-4-sulfide (I). A) Fifteen grams of anhydrous 1,3,5-trimethylpyrazole was heated to 100° in a beaker on a metal bath. Then, 8.5 g of sulfur monochloride was added slowly and dropwise during 10 min. A vigorous evolution of hydrogen chloride was observed. The reaction mixture was allowed to stand at 100-110° for 2 hr, was poured into a mixture of 100 ml of water, 20 ml of concentrated hydrochloric acid, and 1 g of activated charcoal. After boiling for 15 min, the mixture was filtered from the charcoal and sulfur. The filtrate was evaporated to 50 ml, and made alkaline by addition of concentrated ammonia solution until the mixture had a strong smell of ammonia. The oil produced was extracted with benzene, and submitted to vacuum distillation. Yield of (I), 11.1 g (89%) b.p. 216-219° (12 mm). After being recrystallized twice from petroleum ether, (I) melted at 139-140°.

Found %: C 57.89, 57.80; H 7.47, 7.21; S 12.84, 12.56; N 22.61, 22.67. $C_{12}H_{18}N_4S$. Calculated %: C 57.57; H 7.25; S 12.85; N 22.41.

Dipicrate, m.p. 160-161° (from alcohol).

Found %: C 40.85, 40.78; H 3.67, 3.62; N 19.89, 19.62. $C_{12}H_{18}N_4S \cdot 2C_6H_3N_3O_7$. Calculated %: C 40.68; H 3.42; N 19.78.

B) A mixture of 15 g of dry 1,3,5-trimethylpyrazole hydrochloride and 20 ml of freshly distilled thionyl chloride was heated on a boiling water bath for 4 hr in a flask fitted with a reflux condenser, and a calcium chloride guard tube. The reaction product was poured into 50 ml of water, and the mixture was allowed to stand overnight after being made alkaline by the addition of concentrated ammonia solution (until the mixture strongly smelt of ammonia). The crystals, which separated out, were filtered off, and carefully pressed free of oil while washing with water. After two recrystallizations from petroleum ether, the crystals melted at 140°. Yield of the pure sulfide, 3.2 g (26%). This product did not give a m.p. depression when mixed with the substance prepared as described above under A). The picrate (m.p. 161°) behaved in the same way.

The filtrate (containing a heavy oil) was extracted with benzene. Distillation of the benzene extract gave 2.6 g of 1,3,5-trimethyl-4-chloropyrazole, b.p. 113-115° (35 mm), n_D^{20} 1 4922, d_4^{20} 1.1409.

Found %: N 19.37, 19.31. $C_6H_9N_2Cl$. Calculated %: N 19.45.

The picrate of the latter substance melted at 142.0-143.5° and did not depress the melting point of an authentic sample of 1,3,5-trimethyl-4-chloropyrazole picrate (see below).

1,3,5-Trimethyl-4-chloropyrazole (II). A solution of 29.3 g of 1,3,5-trimethylpyrazole hydrochloride in 15 ml of acetic acid was heated on a water bath to 90°, and treated with 20 ml of 30% hydrogen peroxide solution. After the reaction was over, the solution was cautiously treated with ammonia solution until it acquired a smell of ammonia. Then, the resulting mixture was carefully extracted with benzene. Distillation of the benzene extract gave 16.5 g (57%) of 1,3,5-trimethyl-4-chloropyrazole, b.p. 94-95° (18 mm), 111-112° (31 mm), n_D^{20} 1.4920, d_4^{20} 1.1401.

Found %: N 19.28, 19.22. $C_6H_9N_2Cl$. Calculated %: N 19.45.

Picrate, m.p. 142.5-143.5° (from alcohol) [5].

1,3,5-Trimethylpyrazolyl-4-sulfone. A) 1,3,5-Trimethylpyrazolyl-4-sulfide (I) (2.5 g) was suspended in 50 ml of tepid water acidified with 3 drops of acetic acid. Then, the suspension was treated by portions during 1 hr (efficient stirring) with 2.1 g of solid potassium permanganate. The permanganate color faded in approximately 1 hr. The mixture was treated with 50 ml of methanol, heated to boiling, and filtered from the manganese dioxide. The latter was carefully washed with hot methanol. The combined filtrate and washings were evaporated to 15 ml. The crystalline sulfone separated out upon cooling. Yield, 2.8 g (96%), m.p. 99-100° (from water).

Found %: N 19.84, 19.71. $C_{12}H_{18}O_2N_4S$. Calculated %: N 19.86.

Dipicrate, m.p. 104-105° (from water).

Found %: N 18.37, 18.24. $C_{12}H_{18}O_2N_4S \cdot 2C_6H_3O_7N_3$. Calculated %: N 18.40.

When sulfide (I) was oxidized with peracetic acid as described below, the yield of the crude sulfone was only about 25%.

Reduction of 1,3,5-trimethylpyrazolyl-4-sulfone. A solution of 2.82 g of the sulfone in 60 ml of concentrated hydrochloric acid was treated with 7 g of amalgamated zinc, and refluxed until all the zinc had dissolved (about 3 hr). The reaction mixture was made alkaline with sodium hydroxide, and extracted with benzene. After drying with anhydrous magnesium sulfate, the benzene extract was distilled to give 2 g (80%) of the sulfide, m.p. 138-139° (after two recrystallizations from petroleum ether). Dipicrate, m.p. 159-160° (from alcohol). Neither the sulfide, nor its picrate gave a mixed melting point depression with the corresponding compounds prepared as described above.

Reaction of 1,3,5-trimethylpyrazole with thionyl chloride in the presence of aluminum chloride. A mixture of 100 ml of dry carbon tetrachloride and 77.7 g of anhydrous aluminum chloride was treated cautiously at 0-10° with 22 g of 1,3,5-trimethylpyrazole. After cooling the mixture to -5°, 12 g of thionyl chloride was added gradually and dropwise. The reaction mixture was stirred at 10-15° for 1 hr, and then at 20-25° for a further 6 hr. Then, it was cautiously decomposed with 300 g of ice. After making alkaline with excess of solid sodium hydroxide, the mixture was extracted with benzene. Distillation of the benzene extracts gave 2.9 g (11%) of a substance with b.p. 203-205° (8 mm), and m.p. 155-156° (from acetone). mixed melting point with the sulfide (I) showed a depression of 25°.

Found %: C 66.11, 66.04; H 7.55, 7.46; N 25.37, 25.41. $C_{12}H_{18}N_4$. Calculated %: C 66.08; H 8.31; N 25.68.

Dipicrate, m.p. 176-178° (from methanol). Mixed melting point with the picrate of the sulfide (I) showed a depression of 40°.

Found %: C 42.84, 42.72; H 3.55, 3.55. $C_{12}H_{18}N_4 \cdot 2C_6H_3O_7N_3$. Calculated %: C 42.61; H 3.58.

1,3,5-Trimethylpyrazole-4-chlorosulfide. Thirty ml of sulfur monochloride was heated to 100-110°, and treated slowly, and with efficient stirring with 15 g of dry 1,3,5-trimethylpyrazole hydrochloride, added by portions during half an hour. The reaction mixture was heated at 110-120° for a further period of 1.5 hr; then, excess of sulfur monochloride was driven off in vacuum (water pump). The residue was poured into 50 ml of water and heated to 80° for 15 min with vigorous stirring. The mixture thus obtained was treated with 15 ml of a concentrated sodium hydroxide solution, stirred for 10 min at 60-70°, and extracted with ether after cooling. The ethereal extract

was dried with potassium carbonate, and distilled in vacuum. Yield of the chlorosulfide derivative, 6.9 g (39%), b.p. 129-132° (37 mm), m.p. 61-62° (from petroleum ether). This substance appeared as colorless needles with strongly characterized lacrymatory properties.

Found %: C 40.68, 40.64; H 4.97, 4.88; N 15.95, 15.63. $C_6H_9N_2SCl$. Calculated %: C 40.79; H 5.13; N 15.99.

Picrate, m.p. 71-72° (from 70% alcohol).

Found %: C 35.59, 35.48; H 2.97, 2.90. $C_6H_9N_2SCl \cdot C_6H_3O_7N_3$. Calculated %: C 35.52; H 2.93.

Reaction of 1,3,5-trimethylpyrazole hydrochloride with sulfur dichloride. Fifteen grams of 1,3,5-trimethylpyrazole hydrochloride was treated in a flask fitted with a reflux condenser with 5.15 g of SCl_2, the addition being done slowly and dropwise. An extremely vigorous reaction took place, hydrogen chloride being evolved. The reaction mixture was heated on a water bath for 1 hr, and poured into 25 ml of hydrochloric acid (1 : 1). Activated charcoal (0.5 g) was added, and the mixture was filtered off. The filtrate was made alkaline with ammonia, and extracted with benzene. Distillation gave the following products: a) 1.4 g of the starting pyrazole; b) 1.9 g of 1,3,5-trimethyl-4-chloropyrazole, b.p. 105° (22 mm); picrate, m.p. 143° giving no mixed melting point depression when mixed with the above mentioned derivative; c) 2.6 g (22%) of the sulfide (I), b.p. 220-225° (18 mm), m.p. 141° (from petroleum ether), giving no mixed melting point depression when mixed with the sulfide prepared as directed above. Dipicrate, m.p. 161° (from alcohol), giving no mixed melting point depression when mixed with the dipicrate whose preparation has been already described.

1-Phenyl-3,5-dimethylpyrazolyl-4-sulfide (III). It was obtained by the above method upon reaction with sulfur monochloride. Yield, 61%; m.p. 132-133° (from benzene–petroleum ether mixture).

Found %: C 70.82, 70.82; H 6.02, 6.00; N 14.90, 14.80. $C_{22}H_{22}N_4S$. Calculated %: C 70.53; H 5.92; N 14.96.

1-Phenyl-3,5-dimethylpyrazolyl-4-sulfone. A mixture of 1 g of the sulfide (III), 15 ml of acetic acid, and 10 ml of 30% hydrogen peroxide solution was heated on a boiling water bath for 6 hr. The reaction product was poured into 100 ml of water, and the precipitate formed was filtered off. Yield of the sulfone (after recrystallization from petroleum ether), 0.78 g; m.p. 184-185°.

Found %: N 13.75, 13.70. $C_{22}H_{22}O_2N_4S$. Calculated %: N 13.79.

1-Phenylpyrazolyl-4-sulfide was obtained by reaction with sulfur monochloride under the conditions described above. Yield, 57%, m.p. 153° (recrystallized twice from acetone) [4]. This substance did not give a melting point depression when mixed with the sulfide obtained by the reaction with thionyl chloride (see below). It did not form a picrate.

Found %: C 67.81, 67.61; H 4.59, 4.51; N 17.60, 17.50. $C_{18}H_{14}N_4S$. Calculated %: C 67.92; H 4.43; N 17.59.

1-Phenylpyrazolyl-4-sulfone was obtained with a 84% yield by a method of preparation analogous to that used for the synthesis of 1-phenyl-3,5-dimethylpyrazolyl-4-sulfone, m.p. 179° (from alcohol) [4]. It did not depress the melting point of the sulfone prepared by the oxidation of the sulfide which was synthesized with the help of thionyl chloride.

Found %: N 16.47, 16.41. $C_{18}H_{14}O_2N_4S$. Calculated %: N 16.62.

1-Phenylpyrazolyl-4-sulfide. A mixture of 10.6 g of 1-phenylpyrazole and 28 g of freshly distilled thionyl chloride was boiled for 3 hr in a flask fitted with a reflux condenser. Excess of thionyl chloride was driven off, and the residue was decomposed with 200 ml of water. The reaction product was filtered off and carefully pressed to free it from oil. After recrystallization from acetone, 1.6 g (11%) of the sulfide was obtained, m.p. 153°. It did not give a mixed melting point depression with the sulfide previously prepared with the help of sulfur monochloride. It did not form a picrate.

1-Phenylpyrazolyl-4-sulfone was prepared from this sulfide by the peracetic acid method described above. Yield, 88%, m.p. 179° (from alcohol). It did not give a mixed melting point depression with the product already described.

1-Propyl-3,5-dimethylpyrazolyl-4-sulfide was obtained with a 67% yield by the method already described for the preparation of 1,3,5-trimethylpyrazolyl-4-sulfide (with sulfur monochloride), b.p. 225-230° (13 mm). It appeared as a thick oil.

Found %: N 18.51, 18.42. $C_{16}H_{26}N_4S$. Calculated %: N 18.27.

Dipicrate, m.p. 140-141° (from ether).

Found %: N 18.53, 18.58. $C_{16}H_{26}N_4S \cdot 2C_6H_3O_7N_3$. Calculated %: N 18.28.

1-Ethyl-3,5-dimethylpyrazolyl-4-sulfide was obtained by the general method with sulfur monochloride. Yield, 68%, b.p. 202-205° (10 mm), n_D^{20} 1.5475. It appeared as a thick yellow oil.

Found %: N 19.95, 19.90. $C_{14}H_{22}N_4S$. Calculated %: N 20.02.

Dipicrate, m.p. 134-135° (from ether).

Found %: N 19.48, 19.31. $C_{14}H_{22}N_4S \cdot 2C_6H_3O_7N_3$. Calculated %: N 19.07.

Attempt to synthesize 1-phenylpyrazolyl-4-sulfoxide. It was not possible to obtain the sulfoxide by the reaction of 1-phenylpyrazole with thionyl chloride in the presence of aluminum chloride in carbon disulfide or carbon tetrachloride medium. Even when the reaction was carried out at 50° for 6 hr, no product was obtained, except the recovered starting material.

SUMMARY

Pyrazoles display superaromatic properties in their reactions with halogen derivatives of sulfur. The reaction products are the corresponding sulfides of the pyrazole series.

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THE STUDY OF FURAN COMPOUNDS

XIII. FORMATION OF DERIVATIVES OF 1,6-DIOXASPIRO-(4,4)-NON-3-ENE BY ELECTROLYTIC METHOXYLATION OF γ-FURYL ALKANOLS

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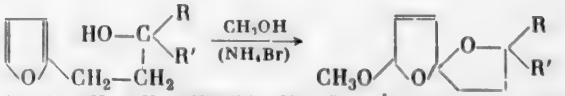
In a previous paper [1] we described the results of experiments on methoxylation of a series of furan compounds with functional groups in the side chain.

The present communication is concerned with electrolytic methoxylation of furan alcohols which contain hydroxyl in the side chain in position 3, that is, γ-furyl alkanols. In undertaking this study, we started from the assumption that because of the spacial nearness of the hydroxyl groups in the side chain to the furan ring in such alcohols, besides the usual processes of intermolecular alkoxylation there would be an intramolecular reaction accompanied by cyclization:

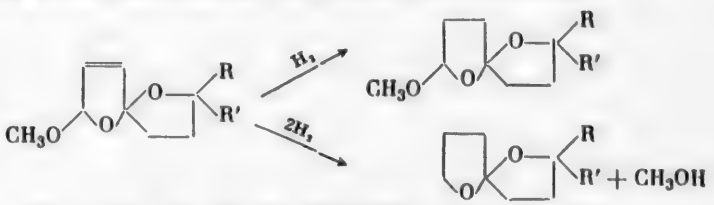


R = H, CH_3, CH_3—$CH(CH_3)_2$, CH_3, C_2H_5, iso-C_5H_{11}; R′ = respectively H, H, H, CH_3, CH_3, CH_3.

This was fully confirmed in the experimental test. It was shown that primary, secondary, and tertiary γ-furan alkanols, namely; 1-(α-furyl)-3-propanol (I), 1-(α-furyl)-3-butanol (II), 1-(α-furyl)-5-methyl-3-hexanol (III), 1-(α-furyl)-3-methyl-3-butanol (IV), 1-(α-furyl)-3-methyl-3-pentanol (V), and 1-(α-furyl)-3,6-dimethyl-3-heptanol (VI), on electrolysis of their solutions in methanol were converted into the corresponding derivatives of 2-methoxy-1,6-dioxaspiro-(4,4)-non-3-ene. The yields reached 76% of the theory which was considerably higher than in all the cases of formation of 1,6-dioxaspiro-(4,4)-nonane and its homologs in the hydrogenation of the corresponding furan alcohols [2-6]. The data on the properties and analyses of the thus obtained six derivatives of 1,6-dioxaspiro-(4,4)-non-3-ene are given in Table 1.

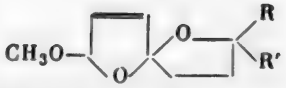
Hydrogenation of the 2-methoxy-1,6-dioxaspiro-(4,4)-non-3-enes under mild conditions (at room temperature, under pressure in the presence of Raney nickel) resulted in formation with yields of up to 90% of the corresponding derivatives of 2-methoxy-1,6-dioxaspiro-(4,4)-nonanes, whose properties and analyses are given in Table 2.

Under more severe conditions (at a pressure of 100-120 atm. at 100-120° in the presence of nickel on kieselguhr) in hydrogenation there occurs not only reduction of the double bond, but also splitting of the methoxyl group. This gives the already known 1,6-dioxaspiro-(4,4)-nonane and its homologs.



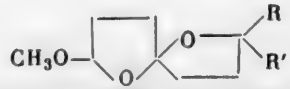
R = H, CH_3, CH_3, C_2H_5; R′ = respectively H, H, CH_3, CH_3.

TABLE 1. Physical Constants and Analyses of 2-Methoxy-1,6-dioxaspiro-(4,4)-non-3-enes



Substance No.	Meaning of R and R'	B.p. (pressure in mm)	n_D^{20}	d_4^{20}	MR_D found	MR_D calc.	Empirical formula	Found (%) C	Found (%) H	Calc. (%) C	Calc. (%) H	M found	M calc.	Yield, %
(VII)	H, H	83—84° (10)	1.4650	1.1093	38.94	39.21	$C_8H_{12}O_3$	61.44, 61.50	7.80, 8.10	61.52	7.75	163.2, 161.8	156.8	53
(VIII)	H, CH_3	72.5—73 (5)	1.4572	1.0587	43.80	43.82	$C_9H_{14}O_3$	63.44, 63.76	8.49, 8.49	63.51	8.30	178.5, 179.3	170.2	76
(IX)	H, $CH_2CH(CH_3)_2$	81 (2)	1.4570	1.0015	57.73	57.68	$C_{12}H_{20}O_3$	67.59, 67.89	9.49, 9.60	67.89	9.49	202.0, 203.7	212.28	75
(X)	CH_3, CH_3	75—77 (7)	1.4518	1.0267	48.38	48.44	$C_{10}H_{16}O_3$	65.46, 65.42	8.70, 8.89	65.19	8.75	183.08, 183.50	184.23	63
(XI)	CH_3, C_2H_5	92.5—93 (6)	1.4563	1.0204	53.06	52.83	$C_{11}H_{18}O_3$	66.73, 66.81	9.25, 9.21	66.64	9.15	195, 199	198.25	65
(XII)	CH_3, iso-C_5H_{11}	103—104 (2)	1.4573	0.9775	66.99	66.91	$C_{14}H_{24}O_3$	69.98, 69.95	10.31, 10.06	69.96	10.07	244.8, 246.1	240.33	35

TABLE 2. Physical Constants and Analyses of 2-Methoxy-1,6-dioxaspiro-(4,4)-nonanes,



Substance No.	Meaning of R and R'	B.p. (pressure in mm)	n_D^{20}	d_4^{20}	MR_D found	MR_D calc.	Empirical formula	Found (%) C	Found (%) H	Calculated (%) C	Calculated (%) H	Yield, %
(XIII)	H, H	77—78° (14)	1.4471	1.071	39.54	39.67	$C_8H_{14}O_3$	60.93, 60.89	8.99, 9.02	60.74	8.92	82
(XIV)	H, CH_3	73—74 (10)	1.4420	1.026	44.41	44.29	$C_9H_{16}O_3$	62.97, 62.47	9.57, 9.33	62.77	9.37	82
(XV)	CH_3, CH_3	73—75 (10)	1.4392	0.9998	49.02	48.91	$C_{10}H_{18}O_3$	64.79, 65.06	9.97, 10.03	65.02	9.74	90
(XVI)	CH_3, C_2H_5	88—89 (10)	1.4447	0.9951	53.53	53.53	$C_{11}H_{20}O_3$	65.73, 65.82	10.24, 10.18	65.97	10.06	79

TABLE 3. Conditions of Alkoxylation of γ-Furyl Alkanols

γ-Furyl alkanol	Amt. of starting substance (g mole)	Current strength, A	Voltage, V	Temp. in cell	No. of ampere-hours
(I)	0.5	4—2	8—26	—14°	35.7
(II)	0.4	4—1.5	5—32	—12	30
(III)	0.22	4—2	11—32	—12	21
(IV)	0.33	4—1.5	8—30	—14	26
(V)	0.3	4—1.5	9—34	—14	28.5
(VI)	0.2	4.5—1.5	10—36	—14	17

Note: In all the experiments we used 230 ml of methyl alcohol. Electrolyte NH_4Br.

The identity of the 1,6-dioxaspiro-(4,4)nonanes obtained by the two methods, from 2-methoxy-1,6-dioxaspiro-(4,4)-non-3-enes and in the hydrogenation of γ-furyl alkanols, was confirmed by the identity of infrared absorption spectra as shown in Fig. 1, and also by the data given in the experimental part. These reactions, along with the data given in Table 1 fully confirm the structure of 2-methoxy-1,6-dioxaspiro-(4,4)-non-3-ene and its homologs.

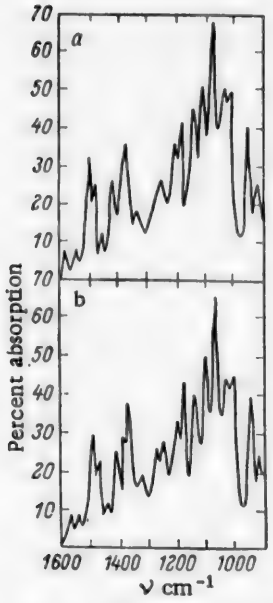


Fig. 1. Infrared absorption spectra of 2-methyl-1,6-dioxaspiro-(4,4)-nonane obtained from 2-methoxy-7-methyl-1,6-dioxaspiro-(4,4)-non-3-ene (a), and in the hydrogenation of 1-(α-furyl)-3-butanol (b)

The infrared absorption spectra in the region 900-1600 cm^{-1} were taken for 2-methyl-1,6-dioxaspiro-(4,4)-nonane, 2-methoxy-7-methyl-1,6-dioxaspiro-(4,4)-nonane (XIV), and 2-methoxy-7-methyl-1,6-dioxaspiro-(4,4)-non-3-ene (VIII) (Fig. 2). In this frequency interval all the three types of substances studied showed a whole series of absorption bands whose position and intensity remained constant and which were evidently characteristic for the spirane ring of 1,6-dioxaspiro-(4,4)-nonane. In addition we could see the very intense bands at 1000-1130 cm^{-1} which did not shift position in the spectra of all the spiranes with methoxyl groups in the molecule (1015, 1065, 1130 cm^{-1}) and were somewhat shifted in the spectrum of 2-methyl-1,6-dioxaspiro-(4,4)-nonane. We should also note that the spectra of compounds of the group of 1,6-dioxaspiro-(4,4)-nonanes recall the spectra of other bicyclic systems very similar in structure [7, 8].

There is still only one method for preparing compounds of the series 2-alkoxy-1,6-dioxaspiro-(4,4)-non-3-enes and 2-alkoxy-1,6-dioxaspiro-(4,4)-nonanes described in this paper. For the synthesis of 1,6-dioxaspiro-(4,4)-nonanes and homologs, the new method of preparation suggested by us gives higher yields than those previously known [2-6, 9, 10] and also reviewed [11], and is more suitable than they are.

EXPERIMENTAL

The preparation of the furan alcohols was described in [2-6, 12, 13]. 1-(α-Furyl)-5-methyl-3-hexanol was obtained by hydrogenation of furfurylidine methylisobutyl ketone in the presence of a copper-chromium catalyst at 120° and 100 atm. Yield 79-80%.

B. p. 116-117° (7 mm), n_D^{20} 1.4715, d_4^{20} 0.9649, MR_D 52.85; calc. 53.032.

Found %: C 72.93, 72.53; H 10.27, 10.25; OH 9.39, 9.35. $C_{11}H_{18}O_2$. Calculated %: C 72.49; H 9.96; OH 9.32.

Electrolysis of the solutions of γ-furyl alkanols was carried out in an electrolyzer with a nickel cathode and a carbon anode whose construction was described previously [1, 14]. A typical procedure for alkoxylation is shown in the following example.

Synthesis of 2-methoxy-7-methyl-1,6-dioxaspiro-(4,4)-non-3-ene (VIII). We dissolved 58.0 g of freshly distilled 1-(α-furyl)-3-butanol (II) and 5.0 g of ammonium bromide in 230 ml of methyl alcohol. The solution was poured into the electrolyzer, cooled to -12° and electrolyzed for nine hours at current strength 4A and voltage 5 V. As the electrolysis proceded the conductivity fell and so, to maintain the necessary current strength the voltage was increased to 30-32 V, and electrolysis was continued until the current at this voltage fell to 1.5-1 A, with the temperature maintained at the level given.

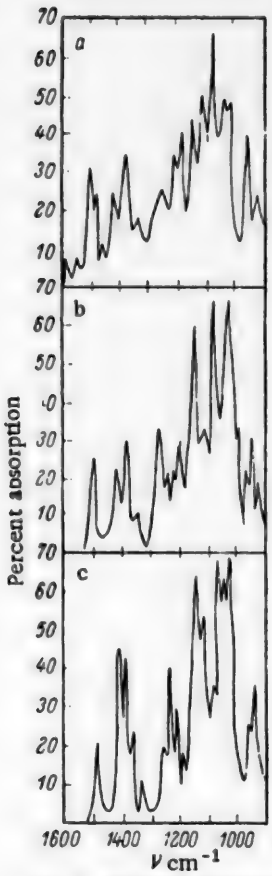


Fig. 2. Infrared absorption spectra of 2-methyl-1,6-dioxaspiro-(4,4)-nonane (a), 2-methoxy-7-methyl-1,6-dioxaspiro-(4,4)-nonane (b), and 2-methoxy-7-methyl-1,6-dioxaspiro-(4,4)-non-3-ene (c).

At the end of the electrolysis the solution was poured into a flask and treated with sodium methylate (1.2 g of metallic sodium and 20 ml of methanol). The methanol and ammonia were distilled off at reduced pressure and the precipitate of sodium bromide which came down was filtered off and washed with ether. The residue after removal of the ether was rectified in a vacuum column with an effectiveness of 12 theoretical plates.

In Table 3 we give data on conditions of experimental alkoxylations.

Hydrogenation of 2-methoxy-1,6-dioxaspiro-(4,4)-non-3-ene and its homologs was carried out in a rotating steel autoclave.

Synthesis of 2-methoxy-7-methyl-1,6-dioxaspiro-(4,4)-nonane (XIV). Twenty g of 2-methoxy-7-methyl-1,6-dioxaspiro-(4,4)-non-3-ene (VIII), 20 ml of anhydrous alcohol, and 1.5 g of Raney nickel were placed in a 150 ml autoclave. The initial hydrogen pressure was 100-120 atm, at room temperature. Hydrogenation ended at absorption of 3 liters of hydrogen. The catalyzate was removed from the autoclave, the catalyst was filtered off and the solvent was distilled off on a water bath. The residue was distilled in a vacuum.

In a similar way we carried out the hydrogenation of 2-methoxy-1,6-dioxaspiro-(4,4)-non-3-ene (VII), 2-methoxy-7,7-dimethyl-1,6-dioxaspiro-(4,4)-non-3-ene (X), and 2-methoxy-7-methyl-7-ethyl-1,6-dioxaspiro-(4,4)-non-3-ene (XI).

Synthesis of 2-methyl-1,6-dioxaspiro-(4,4)-nonane. Twenty g of 2-methoxy-7-methyl-1,6-dioxaspiro-(4,4)-non-3-ene (VIII), 20 ml of anhydrous alcohol, and 2 g of nickel on kieselguhr were placed in a 150 ml autoclave. The initial hydrogen pressure was 100-120 atm, temperature 120°. The hydrogenation product was treated as described above. Yield of 2-methyl-1,6-dioxaspiro-(4,4)-nonane 54%. This was a liquid with a peculiar terpene odor.

B. p. 162-164°, n_D^{20} 1.4427, d_4^{20} 0.9911, MR_D 38.01; calc. 38.03. Literature values, b.p. 162-164°, n_D^{20} 1.4428, d_4^{20} 0.9920 [5].

When 2-methoxy-1,6-dioxaspiro-(4,4)-non-3-ene (VII) was hydrogenated under these conditions we obtained 56% of 1,6-dioxaspiro-(4,4)-nonane (a liquid).

B. p. 82-83° (60 mm), n_D^{20} 1.4489, d_4^{20} 1.020, MR_D 33.16; calc. 33.41. Literature values, b.p. 81-82° (60 mm), n_D^{25} 1.4461, d_4^{25} 1.0341 [3].

From 2-methoxy-7,7-dimethyl-1,6-dioxaspiro-(4,4)-non-3-ene (X) we obtained 65% of 2,2-dimethyl-1,6-dioxaspiro-(4,4)-nonane (a liquid).

B. p. 84-86° (46 mm), n_D^{20} 1.4392, d_4^{20} 0.9618, MR_D 42.74; calc. 42.65.

The spirane obtained in the hydrogenation of 1-(α-furyl)-3-methyl-3-butanol* had b.p. 83-84° (45 mm), n_D^{20} 1.4388, d_4^{20} 0.9597.

From 2-methoxy-7-methyl-7-ethyl-1,6-dioxaspiro-(4,4)-non-3-ene (XI) we obtained 53% of 2-methyl-2-ethyl-1,6-dioxaspiro-(4,4)-nonane (a liquid).

* Carried out by Z. V. Til'.

B. p. 103-104° (45 mm), n_D^{20} 1.4446, d_4^{20} 0.9638, MR_D 46.92; calc. 47.26. Literature values: b.p. 102-104° (45 mm), n_D^{20} 1.4443, d_4^{20} 0.9614 [6].

The infrared absorption spectra were taken on an H-800 spectrophotometer (Hilger) in the region 900-1600 cm^{-1} with a sodium chloride prism. All the substances were studied in the liquid state as a fine film between sodium chloride plates.*

SUMMARY

1. We have shown for the first time that under conditions of electrolytic alkoxylation of primary, secondary, and tertiary γ-furyl alkanols there occurs an intramolecular cyclization, forming good yields of 2-alkoxy derivatives of 1,6-dioxaspiro-(4,4)-non-3-ene.

2. By catalytic hydrogenation of 2-methoxy-1,6-dioxaspiro-(4,4)-non-3-ene and its homologs, depending on the reaction conditions, there is conversion to 2-methoxy-1,6-dioxaspiro-(4,4)-nonane and its homologs, or to 1,6-dioxaspiro-(4,4)-nonane and its homologs.

3. We have worked out new preparative methods for obtaining compounds of these groups, in which 2-methoxy-1,6-dioxaspiro-(4,4)-nonene and 2-methoxy-1,6-dioxaspiro-(4,4)-nonane were not previously known. We have described the properties of the following new compounds: 2-methoxy-1,6-dioxaspiro-(4,4)-non-3-ene and its 7-methyl, 7-isobutyl, 7,7-dimethyl, 7-methyl-7-ethyl, and 7-methyl-7-isoamyl homologs, and also 2-methoxy-1,6-dioxaspiro-(4,4)-nonane and its 7-methyl, 7,7-dimethyl, and 7-methyl-7-ethyl homologs. We have described the process for obtaining the previously unknown 1-(α-furyl)-5-methyl-3-hexanol.

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All abbreviations of periodicals in the above bibliography are letter-by-letter transliterations of the abbreviations as given in the original Russian journal. *Some or all of this periodical literature may well be available in English translation.* A complete list of the cover-to-cover English translations appears at the back of this issue.

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* Carried out by A. D. Peshekhonova.

THE SYNTHESIS OF TRANS-p,p'-DIPHENYLSTILBENE

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At the present time p,p'-diphenylstilbene (DPS) is used in scintillation technique [1].

There is evidence in the literature of the possibility of its synthesis by pyrolysis of polythio-p-phenylbenzaldehyde, from which DPS is obtained with m.p. 295° (302-305°) [2]; however, no description of the synthesis is given.

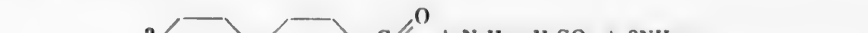
Recently E. E. Baroni and G. Bushbek [3] have described the preparation of DPS from p,p'-diphenyl benzoin by a method analogous to the preparation of stilbene from benzoin [4]; however, the m.p. (222-223°) does not agree with the m.p. of DPS obtained by pyrolysis [2].

This can be explained by the fact that, as is well known, in the preparation of ethylene derivatives cis- and trans-isomers can be formed, and the amount of one or the other isomer depends on the method of preparing the substituted ethylene. Thus, for example, in the synthesis of stilbene by the reduction of benzoin there are formed about 40% cis-stilbene (an oily liquid) and 60% trans-stilbene (colorless crystals).

As we have shown, in the synthesis of stilbene by thermal decomposition of benzaldehyde only trans-stilbene is obtained.

As a result of the work discussed above [3] the DPS was evidently obtained in the cis-form.

Based on the experiments on obtaining trans-stilbene, we have work out the synthesis of DPS by thermal decomposition of p,p'-diphenylbenzalazine.

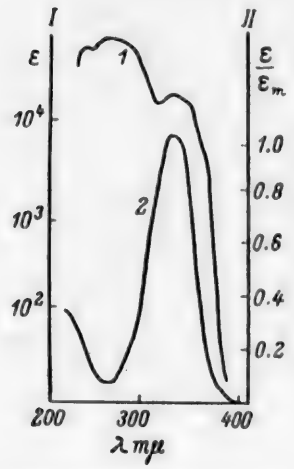


The starting product is diphenyl, from which by the known method [5] we synthesized p-phenylbenzaldehyde.

When a hydrazine hydrate solution is treated with a solution of p-phenylbenzaldehyde, p,p'-diphenylbenzalazine is formed. The latter when decomposed thermally loses nitrogen and gives DPS. In the crystalline state and in organic solvents in ultraviolet light this has a strong blue fluorescence; m.p. 295°, which agrees with the literature value [2].

The presence of a strong fluorescence in the DPS obtained in [3] suggests that, besides the chief mass of cis-DPS there is an admixture of the trans-form. This is confirmed by comparison of the absorption spectra in dioxane. Thus the absorption spectrum of DPS obtained in [3] has a chief absorption maximum at λ 280 mμ and a weak maximum at λ 340 mμ (figure, curve 1). The spectrum of our DPS has one clear absorption band at λ 340 mμ (figure, curve 2).

Considering that in both cases there were carried out elementary analysis of the substances which were obtained and that they were DPS ($C_{26}H_{20}$) we suggest that the absorption maximum in dioxane for cis-DPS is λ 280 mμ and for the trans-form, λ 340 mμ. The presence of the weak absorption maximum at λ 340 mμ in the DPS in [3] indicates the presence in it of an admixture of trans-DPS. The presence of absorption maxima in the cis- and trans-DPS (at λ 280 mμ and 340 mμ) also agrees with the known fact [6] that the absorption maximum of a trans-form of stilbene in shifted to the long wave side as compared to the cis-form.



Absorption spectra of p,p'-diphenylstilbenes in dioxane. 1) Obtained in the work of E. E. Baroni and G. Bushbek; 2) trans-configuration obtained in the present work.

EXPERIMENTAL

p-Phenylbenzaldehyde. The synthesis was carried out by the Gattermann reaction [2]. The experiments showed that there is no need to obtain pure p-phenylbenzaldehyde for the synthesis of the azine. The technical aldehyde was dissolved in dichloroethane and was used further in the form of the solution.

p,p'-Diphenylbenzaldehyde. We mixed 189 g of hydrazine sulfate (technical 75%) with 169 ml (154 g) of 25% ammonia and 1100 ml of water; the mass was stirred to full solution of the hydrazine sulfate and then a solution of 330 g of technical p-phenylbenzaldehyde in 600 ml of dichloroethane was added through a dropping funnel in the course of four hours with stirring; stirring was continued for two hours more. The resulting p,p'-diphenylbenzalazine in the form of a brown mass was purified by boiling for 30 minutes with 300 ml of benzene, was cooled, filtered, washed on the filter with two portions of 50 ml of cold benzene, and was dried at 70-80°.

The resulting technical p,p'-diphenylbenzalazine was a yellow powder with m.p. 230-245° (the literature gives 245° [7]); it was not further purified but was used for the decomposition.

p,p'-Diphenylstilbene (DPS). Thermal decomposition of p,p'-diphenylbenzalazine was carried out in a 1 liter steel reactor. Decomposition of 290 g of azine was run at 300-350° for two hours. The resulting DPS was purified by boiling for 30 minutes with 200 ml of benzene, filtering and washing on the filter with two 50 ml portions of cold benzene. The substance was a yellow powder which was three times recrystallized from chlorobenzene (100 g of chlorobenzene per g of substance); the first recrystallization was carried out with the addition of activated charcoal, the second with activated alumina. Greenish yellow scales, m.p. 295°. Yield 35 g (13%). Very difficultly soluble in organic solvents.

Found %: C 94.06; H 5.94. $C_{26}H_{20}$. Calculated %: C 93.92; H 6.08.

SUMMARY

We have worked out the synthesis of trans-p,p'-diphenylstilbene by thermal decomposition of p,p'-diphenylbenzalazine and have confirmed its trans-configuration.

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SPATIAL STRUCTURE AND REACTIVITY

XIX. THE SYNTHESIS OF AMINO DERIVATIVES OF BENZOPHENONE AND THE KINETICS OF THEIR ACYLATION

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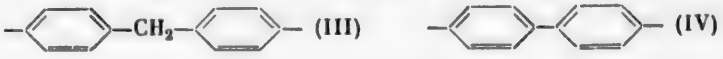
In one of the previous communications of this series [1] we studied the kinetics of the reaction of 4-aminodiphenyl methane (I) and 4-amino-4'-nitrodiphenyl methane (II) with p-nitrobenzoyl chloride and picryl chloride in benzene. We showed that the effect of the 4'-nitro group on the rate of acylation of the 4-amino group was transmitted in the molecular system of diphenyl methane (III), which contained a bridging methylene group, much less intensively than occurred in the case of a biphenyl system (IV) where the benzene rings were joined to each other directly. As shown in previous reports, the degree of transfer of the effect of the 4'-substituent on the reactivity of the functional group in the 4-position in the molecular systems



such as (III) and (IV) could be characterized quantitatively by the ratio of the rate constants for the reaction of mono- and disubstituted derivatives, for example K_I/K_{II} (factor f).

In the present communication we have set ourselves the problem of studying from the above view point the properties of structurally related compounds in which the bridging methylene group is replaced by the carbonyl group. For this purpose we have studied the kinetics of the reaction of 4-aminobenzophenone (V) and 4-amino-4'-nitrobenzophenone (VI)

with p-nitrobenzoyl chloride and picryl chloride in benzene solution. Since substance (VI) is difficult to obtain and since after one of our papers [2] which concerned its structure there appeared the paper of Tsekhanskii [3], we have worked out a completely satisfactory method for preparing this interesting compound, from which its structure is clearly evident. The latter agrees fully with the conclusions drawn earlier in this respect [2].

EXPERIMENTAL

I. Preparation and Purification of the Starting Substances

Synthesis of 4-amino-4'-nitrobenzophenone by partial reduction of 4,4'-dinitrobenzophenone. a) 4,4'-Dinitrobenzophenone was obtained by the method of Städel which we improved [4]. To a solution of 4 g of 4,4'-dinitrodiphenylmethane [2] in 100 ml of boiling glacial acetic acid we added gradually and with shaking a solution of 6.2 g of CrO_3 in 100 ml of the same acid. The rate of addition of oxidizing solution was regulated so that the reaction was not too violent. After addition of all the oxidant, boiling was continued for five hours more. When the dark green solution was cooled, the crystals were filtered off and carefully washed. A further amount of the reaction product was precipitated from the mother liquor by water. Yield 3.8 g (90%); m.p. 189-190°.

b) 4-Amino-4'-nitrobenzophenone. To a solution of 0.5 g of 4,4'-dinitrobenzophenone in 5 ml of boiling pyridine was added 5 ml of a 1 M solution of sodium disulfide in aqueous pyridine [5]. After boiling for 30 minutes, the solution was poured into ten times its volume of cold water. The flakey precipitate settled well and then was

TABLE 1. Kinetics of the Reaction of Amino Derivatives of Benzophenone with p-Nitrobenzoyl Chloride (PNBC) and Picryl Chloride (PC) (In all experiments, a was 0.004545 M and b 0.009090 M)

50°			70°		
$t_{\frac{1}{2}}$ (min)	yield, %	k_2 (liter/mole·sec)	$t_{\frac{1}{2}}$ (min)	yield, %	k_2 (liter/mole·sec)
4-Aminobenzophenone + PNBC					
30	20	0.0158	12	17.9	0.0353
50	29.8	0.0161	20	27.7	0.0372
80	39.8	0.0157	30	37.0	0.0380
120	50.0	0.0158	45	47.9	0.0397
180	59.0	0.0152	65	57.2	0.0399
4-Amino-4'-nitrobenzophenone + PNBC					
240	21.1	0.00212	45	11.8	0.00570
360	28.6	0.00211	90	20.0	0.00539
540	36.7	0.00204	150	30.2	0.00561
840	47.7	0.00206	240	41.4	0.00572
1440	61.4	0.00210	360	50.5	0.00550
4-Aminobenzophenone + PC					
120	13.0	0.00237	40	12.5	0.00697
210	20.9	0.00239	75	21.6	0.00714
360	30.9	0.00236	120	31.2	0.00733
540	40.7	0.00241	180	41.8	0.00777
4-Amino-4'-nitrobenzophenone + PC					
720	10.7	0.000315	240	11.4	0.00104
1440	18.1	0.000292	495	23.0	0.00117
2130	24.6	0.000291	720	29.3	0.00112

filtered off and carefully washed with water. Yield of crude product 0.22 g (50%). It was dissolved in boiling 25% sulfuric acid and on cooling precipitated the sulfate which was decomposed by stirring with aqueous ammonia; the free base, after being washed with water, was recrystallized once from water and benzene. M.p. 180-181°. Mixed with the product previously obtained by treatment of 4,4'-dinitrodiphenylmethane with sodium sulfhydrate [2] it gave no melting point depression.

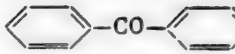
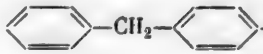
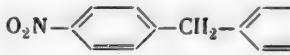
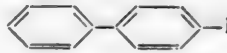
Synthesis of 4-amino-4'-nitrobenzophenone from 4-amino-4'-nitrodiphenylmethane. a) 4-Acetamino-4'-nitrodiphenyl-methane. To a solution of 3.42 g of 4-amino-4'-nitrodiphenylmethane in 15 ml of glacial acetic acid at room temperature was gradually added 1.7 g of acetic anhydride. After standing for one hour, the crystals which precipitated were filtered off and washed with water. Yield 3.96 g (98%). M.p. 165°; this did not change after recrystallization of the substance from glacial acetic acid and alcohol. The acetyl derivative had a yellowish green color; it dissolved well enough in the usual organic solvents, was difficultly soluble in benzene, and insoluble in water; it has not been described in the literature.

Found %: N 10.25, 10.21. $C_{15}H_{14}O_3N_2$. Calculated %: N 10.37.

b) 4-Acetamino-4'-nitrobenzophenone was obtained by oxidation of the preceding product by the method in every way similar to that used for the synthesis of 4,4'-dinitrobenzophenone: a mixture of a solution of 1.6 g of 4-acetamino-4'-nitrodiphenylmethane in 40 ml of glacial acetic acid and 2.4 g of CrO_3 also in 40 ml of glacial acetic acid was boiled for three hours. The reaction product after cooling was precipitated with water. Yield 1.2 g (71%), m.p. 203°. After recrystallization from dilute (1 : 1) alcohol, m.p. 205°. The almost colorless substance dissolved moderately in the usual organic solvents, was difficultly soluble in benzine, and insoluble in water; it has not been previously described.

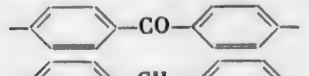
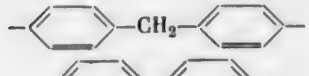
Found %: N 9.76, 9.68. $C_{15}H_{12}O_4N_2$. Calculated %: N 9.86.

TABLE 2. Collected Data on Reaction Kinetics of Amines with p-Nitrobenzoyl Chloride (PNBC) and Picryl Chloride (PC)

Amine	Electrophilic reagent	$K_{25°}$ (liter/mole·sec)	$K_{50°}$ (liter/mole·sec)	$K_{70°}$ (liter/mole·sec)	E_A (cal/mole)	lg A	ΔS# (cal/degree mole)
	PNBC	0.00440•	0.0157 ± 0.0003	0.0380 ± 0.0014	9700	4.78	— 8.8
	PC	0.000475•	0.00238 ± 0.00003	0.00730 ± 0.00028	12400	5.73	—34.7
	PNBC	0.000506•	0.00209 ± 0.00005	0.00560 ± 0.00013	10900	4.66	—39.4
	PC	0.0000453•	0.000299 ± 0.000013	0.00111 ± 0.00007	14500	6.25	—32.1
 [1]	PNBC	0.990 ± 0.020	2.16 ± 0.03	—	6000	4.37	—40.6
	PC	0.338 ± 0.007	0.847 ± 0.015	—	7000	4.68	—39.2
 [1]	PNBC	0.228 ± 0.005	0.501 ± 0.012	—	6000	3.78	—43.3
	PC	0.0567 ± 0.0007	0.158 ± 0.004	—	7800	4.51	—40.0
 [5]	PNBC	0.533 ± 0.010	1.11 ± 0.02	—	5600	3.85	—42.8
	PC	0.0744 ± 0.0021	0.235 ± 0.003	—	8800	5.32	—36.2
[5]	PNBC	0.0505 ± 0.0011	0.118 ± 0.003	—	6500	3.46	—44.7
	PC	0.00548 ± 0.00018	0.0205 ± 0.0009	—	10000	5.15	—37.1
[5]	PNBC	0.580 ± 0.018	—	—	—	—	—
	PC	0.120 ± 0.002	0.394 ± 0.005	—	9100	5.75	—34.3

• Calculated from the value of the rate constant for 50° and 70° by the Arrhenius equation.

TABLE 3. Value of the Factor f for Different Molecular Systems

Molecular system	$f_{25°}$ for the reaction with p-nitrobenzoyl chloride	$f_{25°}$ for reaction with picryl-chloride
	8.70	10.5
	4.34	5.96
	10.6	13.6

c) 4-Amino-4'-nitrobenzophenone. To 1.2 g of 4-acetamino-4'-nitrobenzophenone was added about 75 ml of 50% sulfuric acid and the mixture was heated on a water bath to full solution of the acetyl derivative. The solution was cooled and treated with an equal volume of water, filtered, and the amine was precipitated with ammonia solution. The yield was quantitative; m.p. 178°; after recrystallization from ethanol and then from benzene this was raised to 180-181°. The mixture of this amine with a sample obtained by partial reduction of 4,4'-dinitrobenzophenone and from 4,4'-dinitrodiphenylmethane by the action of sodium sulfhydrate on it [2] gave no melting point depression.

It is clear from these facts that the structure assigned to this product (obtained by the action of sodium hydrosulfide on 4,4'-dinitrodiphenylmethane) or a hydrazo compound of 4-amino-4'-nitrodiphenylamine [3] is an obvious error.

Synthesis of 4-aminobenzophenone. This amine was obtained by the method described in the literature [6] and was further recrystallized twice from ethanol (the first time with activated charcoal) and benzene. M.p. 124°.

Purification of the starting substances. Benzene, p-nitrobenzoyl chloride, and picryl chloride were purified as described previously [5]. The purification of the amino compounds was described in the corresponding method of synthesis. If the preparations were kept for a long time, it was advisable to recrystallize them from benzene.

Method of Kinetic Measurement and Results

The method of measurement of the reaction rates and also the method of calculating and evaluating the accuracy of the second order rate constant, energy of activation according to Arrhenius (E_a), frequency factor (A), and entropy of activation ($\Delta S^{\#}$) were described previously [5]. In all the experiments, as in the previous work, the initial concentration of the acid chloride (a) was half that of the amine (b). In view of the slowness of the reaction of 4-amino-4'-nitrobenzophenone with acid chlorides, and its limited solubility in benzene, the mixture of reacting components was so chosen as to obtain the maximum possible initial concentration of the given amine in solution. For this purpose, in each experiment 10 ml of 0.01 M solution of amine was mixed with 1 ml of 0.05 M solution of acid chloride. Each kinetic measurement was carried out twice.

All the experiments were run at 50 and 70°. The values of the rate constant at 25° needed for comparison with the other data were obtained by calculation using the Arrhenius equation.

In order to test the accuracy of this operation, we determined experimentally the rate constant of the reaction of 4-aminobenzophenone with p-nitrobenzoyl chloride at 25°. This was 0.0047 liter/mole · sec, which agreed well with the value of 0.0044 liter/mole · sec calculated by the Arrhenius equation (see Table 1).

These numerical results on the kinetics of the reaction being considered are given in expanded form in Table 1, where k_i is the average value of the rate constant from two measurements for each time interval t_i. The average value of the rate constants in all the reactions measured (K) is given in the collective Table 2 where we also give values for E_a, A, and $\Delta S^{\#}$ for the reactions studied here and values of the kinetic parameters for some of the reactions which we studied previously.

Discussion of Kinetic Results*

Comparison of the reaction rates of aniline and 4-aminobenzophenone shows that the para-substituent of the type C_6H_5-CO- introduced into the aniline molecule sharply lowers the reactivity of the amine group in the aromatic ring. This demonstrates the clear electron acceptor property of this substituent. This is also illustrated by the results of comparison of the reaction rate of the amino derivatives of benzophenone and diphenylmethane.

In Table 3 we give values for the factor f for the molecular systems benzophenone, diphenylmethane, and biphenyl. It is clear from these results that transmission of the effect of the 4'-nitro substituent on the reactivity of the functional 4-amino group in the molecule of the benzophenone system occurs with less intensity than in the biphenyl system in which the benzene rings are directly connected. There is every reason to suppose that transmission of electron activity from one ring to the other in the benzophenone molecular system as in the case of the previously studied diphenylmethane system [1] depends chiefly on the action of an inductive mechanism. However, the fact that the value of f is markedly higher for the benzophenone system gives reason to suppose that the two following reasons explain the definite positive effect on the conduction in this system. First, the plane of the benzene rings in benzophenone and its derivatives in solution (in the absence of steric hindrance) clearly has a tendency to approach the coplanar configuration [7], as is known so that there appears to some extent an effect of conjugation between the benzene rings in such a system. Second, the π-electrons of the carbonyl group, perhaps, to a definite extent in this case play the role of a free electron pair such as is found in unsaturated hydrocarbons [8, 9]; we previously showed that a free electron pair in a bridge atom could transmit the electron effects from one benzene ring to another through the linking bridge [10, 11].

We should note that in the cases studied by us the value of f for reaction with picryl chloride has a somewhat greater size than in the case of reaction with p-nitrobenzoyl chloride. This is explained by the especially high sensitivity of the first reaction to structural changes in the amine molecules [12].

The relatively energetic parameters of the reactions studied here show that they occur with low E_a and $\Delta S^{\#}$ and for the reaction of the different amines it is natural to note a lesser change in $\Delta S^{\#}$ than in E_a.

SUMMARY

On the basis of a study of the kinetics of the reaction of 4-aminobenzophenone and 4-amino-4'-nitrobenzophenone with p-nitrobenzoyl chloride and picryl chloride in benzene we can come to the following conclusions.

1. The molecular system of benzophenone causes the effect of the 4'-nitrosubstituent on the functional 4-amino group to be weaker than in the biphenyl system, in which the benzene rings are directly connected to each other.

2. The transmission of the electron effect occurs in the benzophenone molecular system from one benzene ring to the other through a bridging carbonyl group chiefly by an inductive mechanism which, perhaps, is connected to some extent with the effect of conjugation which depends on the reaction of the π-electrons of the carbonyl group and the benzene ring, which should also be favored by the almost coplanar configuration of this molecular system.

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* See collective Table 2.

THE TRANSFORMATION OF 2-CHROMONECARBOXYLIC ACIDS INTO 4-CHLOROCOUMARINS

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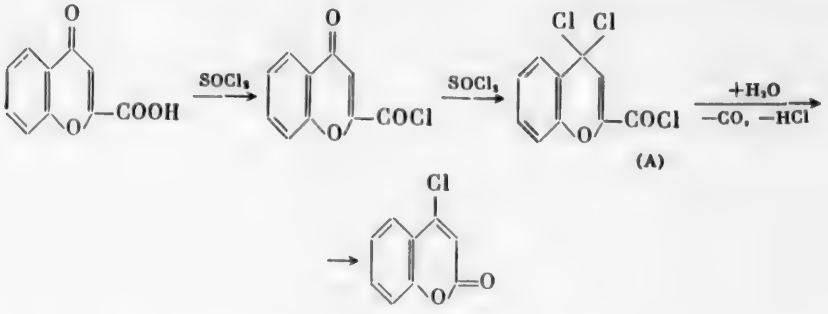
In previous communications [1-3] we reported that 2-chromonecarboxylic acid was converted smoothly to 4-chlorocoumarin by the action of thionyl chloride with later decomposition by water of the intermediate acid chloride of 4,4-dichloro-2-chromencarboxylic acid (A). The trichloride (A) could be isolated in the free form.



Along with the 4-chlorocoumarin (about 90%) there was always formed some of the starting 2-chromonecarboxylic acid (about 10%).

In one of the communications [3] we confirmed the suggestion that the trichloride (A) could react with nucleophilic reagents (water, alcohol) by two paths: toward formation of 4-chlorocoumarin, with accompanying decarboxylation, and by complete solvation of the trichloride to the chromonecarboxylic acid or its ester (in the case of reaction with alcohol).*

Alcohols, as distinguished from water, converted the trichloride (A) into 4-chlorocoumarin only to the extent of 15-20%; most of the trichloride was converted into the corresponding ester of chromonecarboxylic acid (75-80%).

Previously we were unable to change in any marked degree the ratio of reaction products of the trichloride with water (water solutions of sodium hydroxide and sodium bicarbonate, water-dioxane solutions). As a supplement to this work we established that increase in temperature (to 80°) also did not change the character of the reaction.

Continuing the search for conditions which would affect the quantitative ratio of products of splitting of the trichloride (A), we observed that a strong shift in the relative yields of the final products occurred when the decomposition was produced in strong mineral acids (see Table 1). Dilute acids increased the yield of 4-chlorocoumarin. Thus, here we meet with a very interesting relation of the direction of splitting of trichloride (A) to the acidity of the medium. Probably, with increasing acidity of the medium (for mineral acids) there is an increase in rate of hydrolysis chiefly of the halogen of the acid chloride group. The resulting 4,4-dichloro-2-chromenecarboxylic acid is not here in a condition to be decarboxylated by the action of water.

In order to establish the connection of the introduction of substituents in the 2-chromonecarboxylic acid with the ease of conversion of the chromone system into coumarin, we followed this reaction in 6-methyl-, 6-chloro-, 6-bromo-, 6-nitro-, 7-methoxy-, 6,8-dibromo-, 3-methyl-, and 3-phenyl-2-chromonecarboxylic acids.

* The possibility of anionotropic tautomerism for the trichloride (A) was discussed previously [3].

TABLE 1. Effect of Medium on Direction of Decomposition of the Acid Chloride of 4,4-Dichloro-2-chromonecarboxylic Acid (A)

Condition of decomposition*	Relative yield, %**	
	4-chloro-coumarin	2-chromone-carboxylic acid
Water 25 ml, about 80°	95.6	4.4
20 ml acetone + 4 ml water	95.4	4.6
10 ml acetone + 0.54 ml water	92.8	7.2
Solution of NaCl + KNO_3 (3.6 g NaCl + 3 g KNO_3 in 10 ml water), 10 ml	84.3	15.7
75% sulfuric acid, 10 ml	6.7	93.3
63% sulfuric acid, 10 ml	22.5	77.5
56% sulfuric acid, 10 ml	30.2	69.8
47% sulfuric acid, 10 ml	70.8	29.2
80% phosphoric acid, 10 ml	22.6	77.4
Concentrated hydrochloric acid, 10 ml	63.7	36.3

* Trichloride (A) was prepared without isolation in the pure form by the action of thionyl chloride on 2-chromonecarboxylic acid (boiling ten hours). In each experiment the amount of trichloride (A) corresponded to 0.01 mole of acid.

** The total yield of decomposition product was 90-96%.

The syntheses of 6-methyl-, 6-chloro-, 6-nitro-, 7-methoxy-, 6,8-dibromo-, and 3-methyl-2-chromonecarboxylic acids were reported previously [12].

3-Methyl-2-chromonecarboxylic acid, obtained by the condensation of 2-hydroxypropiophenone with diethyl oxalate under the influence of sodium ethylate [12] had a m.p. of 231.5°. In a patent [13] for this same acid synthesized by reaction of ethyl ethoxydichloroacetate with 2-hydroxypropiophenone the m.p. was given as 170°. In order to verify our data we prepared this acid by method [14] by reaction of ethoxalyl chloride with hydroxypropiophenone. Both forms of acid showed the same melting point and properties. 3-Methyl-2-chromonecarboxylic acid [12] had an ultraviolet spectrum curve like the curve for chromones [15]. The substituted 4-chlorocoumarins which were obtained are given in Table 2. As the chlorinating agent we used thionyl chloride or in the case of a particularly slowly reacting acid (IV, VI), phosphorus pentachloride.

The introduction of an electronegative substituent in the benzene ring, and also a methyl or phenyl radical in position 3 of the pyrone ring greatly decreased the rate of transformation of chromonecarboxylic acid into trichloride of type (A); here obviously the slower step is not the formation of acid chloride, but the replacement of the carbonyl by the halogen atoms.

We further studied the effect of substituents in the benzene and pyrone rings of the trichloride on relative yield of the corresponding 4-chlorocoumarins and chromonecarboxylic acids.

In the case of unsubstituted 2-chromonecarboxylic acid we showed that a suitable chlorinating agent, besides $SOCl_2$, PCl_5, and $POCl_3$ [3] is oxalyl chloride (28 hours boiling, yield of 4-chlorocoumarin 88%).

Until recently [1] the acid chloride of 2-chromonecarboxylic acid had not been described. γ-Pyrone-2-carboxylic acids in special cases (for example 5-methoxypyrone-2-carboxylic acid [4]) were converted into acid chlorides. According to patent information [5] the acid chloride of 2-chromonecarboxylic acid was synthesized with thionyl chloride. Under the conditions chosen (a great excess, 27 moles, of thionyl chloride heating to boiling of the solution) there was no exchange of the carbonyl oxygen in position 4 by two chlorine atoms. The recommendation

TABLE 2. Substituted 4-Chlorocoumarins

Substance No.	Substituent in 4-chloro-coumarin	Reaction conditions (amount of chlorinating agent per 0.01 mole chromone carboxylic acid, temperature and time of the reaction)	Yield, %	M.p. h	Empirical formula	% Halogen (total)	
						found [a]	calculated
(I)	6-CH_3	5 ml $SOCl_2$, boiling, 8 hours	79.4	117.5-118°	$C_{10}H_7O_2Cl$	32.86	32.98
(II)	6-Cl	5 ml $SOCl_2$, boiling, 20 hours	70	165-166.5	$C_9H_4O_4Cl_2$	17.96[b]	18.22
(III)	6-Br	10 ml $SOCl_2$, boiling, 30 hours	72.9	169-169.5	$C_9H_4O_2ClBr$	44.18[c]	44.45
(IV)	6-NO_2	8.4 g PCl_5, 5 ml $POCl_3$, 100°, 30 hours	54	168-169	$C_9H_4O_4NCl$	15.60[d]	15.72
(V)	7-CH_3O	4.2 g PCl_5, 5 ml $POCl_3$, 100°, 12 hours[e]	69	137-137.5	$C_{10}H_7O_3Cl$	16.62	16.84
(VI)	6,8-Br_2	8.4 g PCl_5, 5 ml $POCl_3$, 100°, 35 hours	72.5	148.5-150	$C_9H_3O_2Br_2Cl$	57.74[f]	57.70
(VII)	3-CH_3	5 ml $SOCl_2$, boiling, 35 hours	65	119-120[g]	$C_{10}H_7O_2Cl$	18.09	18.22
(VIII)	3-C_6H_5	5 ml $SOCl_2$, boiling, 35 hours	74.2	194-195.5	$C_{15}H_9O_2Cl$	13.98	13.81

Notes: [a] Average of two determinations; [b] Found %: C 61.87; H 3.65. Calculated %: C 61.71; H 3.62. [c] Found%: C 41.66; H 1.58. Calculated %: C 41.65; H 1.55. [d] Found %: N 6.10. Calculated %: N 6.21. [e] with $SOCl_2$ the substance was obtained with poor quality; [f] Found %: C 31.89; H 0.91. Calculated %: C 31.94; H 0.89; [g] According to [11] m.p. 116°. [h] (I) from ligroin and alcohol; (II), (III), (IV), (VII), (VIII) from alcohol; (V) from aqueous CH_3COOH and ligroin; (VI) from alcohol and ligroin.

to take a great excess of thionyl chloride can be considered sound. In our experiments, decreasing the amount of thionyl chloride (to 9 moles without a solvent) caused an appearance of 4-chlorocoumarin after decomposition of the reaction product by water. If the acid chloride is prepared by our process in dichloroethane [1], but the reaction is carried only to solution of the acid, 10% of 4-chlorocoumarin is formed. The acid chloride after recrystallization from ligroin had m.p. 107-108° (yield 83%).

We have previously [2] established the full identity of the forms of 4-chlorocoumarin obtained by rearrangement of the 2-chromonecarboxylic acid and, according to the literature, from 4-hydroxycoumarin by the action of $POCl_3$. However, the identity of these forms of the substance still does not determine their structure accurately as 4-chlorocoumarin. In fact, in our case and in the reaction of 4-hydroxycoumarin with chlorinating agents in pyridine there is possible the formation not of 4-chlorocoumarin, but of 2-chlorochromone. The idea of the probability of conversion of 4-hydroxycoumarin into 2-chlorochromone under the influence of such reagents as phosphorus pentachloride or phosphorus oxychloride comes from the fact that 4-hydroxycoumarin is tautomeric with 2-hydroxychromone [6-8]. There is evidence of the replacement of the hydroxy group by chlorine, for example in 2,6-dihydroxy-4-pyrone [9].

For confirmation of the structure of 4-chlorocoumarin we took its infrared spectrum which had a frequency 5.78 μ (carbonyl group).* According to [10]: in coumarins and chromones the frequency of the C = O group is 5.70-5.90 and 6.00-6.10 μ respectively.

* The spectrum was taken on an IKS-12 apparatus with a sodium chloride prism.

Further evidence for the structure 4-chlorocoumarin is that with sodium methylate it gives 4-methoxycoumarin [2] analogous in melting point (124.5°) to that obtained by methylation of 4-hydroxycoumarin by diazomethane [6-8]. The isomeric 2-methoxychromone formed along with 4-methoxycoumarin by the action of diazomethane on 4-hydroxycoumarin differs from 4-methoxycoumarin in melting point (108°) and chemical properties (it forms a hydrochloride).

Since the conversion of 2-chromonecarboxylic acid into 4-chlorocoumarin is a new and unusual process it was very important to establish the relation of arrangement of substituents in the starting acid and the obtaining of 4-chlorocoumarin. This was done by reduction of 4-chloro-7-methoxycoumarin into the known 7-methoxycoumarin. The absence of a transposition of position 1 and 4 in the pyrone ring during rearrangement was also shown by the identity (in melting points) of our form of 4-chloro-3-methylcoumarin with the preparation described in the literature (synthesized by the reaction of 4-hydroxy-3-methylcoumarin with phosphorus pentachloride [11].

EXPERIMENTAL

3-Phenylchromone-2-carboxylic acid. a) To a solution of sodium ethylate in anhydrous ethanol (from 0.46 g of sodium and 12 ml of ethanol) was added a warm solution of 2.12 g of benzyl-o-hydroxyphenyl ketone and 2.19 g of diethyl oxalate. The mixture was heated for five hours at 60-70° and was cooled. We added 2.8 ml of concentrated hydrochloric acid, boiled for 30 minutes, then added water and extracted with benzene. The benzene was distilled off, the residue was distilled for four hours with a mixture of 4 ml of acetic acid and 2 ml of concentrated acid. The volatile acids were distilled in a vacuum and the residue was dissolved in benzene. The benzene solution was extracted with aqueous bicarbonate which when acidified with hydrochloric acid gave 1.07 g (40%) of 3-phenylchromone-2-carboxylic acid with m.p. 213.5° (from dichloroethane and acetic acid); according to [16], m.p. 212-213°.

With 1 mole of ethylate, condensation took place very poorly.

b) In obtaining the acid by the known method [16] we modified it so that the mixture of benzyl-o-hydroxyphenyl ketone (2.11 g), ethoxalyl chloride (2.5 ml), and pyridine (20 ml) was boiled for one hour, poured into excess aqueous acetic acid, extracted with benzene, and the residue after distillation of the benzene was hydrolyzed as before. Yield 47%. In carrying out the condensation at 20° for 16 hours as described in [16], the yield was not changed.

3-Methylchromone-2-carboxylic acid. We boiled 2.4 g of hydroxypropiophenone, 2.2 g of ethoxalyl chloride, and 6 ml of pyridine for two hours, poured the reaction mass into a mixture of concentrated hydrochloric acid and ice, and extracted with benzene. From the benzene solution, as in the case of 3-phenylchromone carboxylic acid, after hydrolysis we obtained 1.55 g (47%) of 3-methyl-2-chromonecarboxylic acid with m.p. 231-231.5°; a mixture with the acid obtained previously [12] gave no melting point depression.

Increasing the amount of hydroxypropiophenone to 4 g and decreasing the time of heating to 30 minutes [14] lowered the yield of acid.

For 3-methyl-2-chromonecarboxylic acid [12] λ_{max} in mμ (in alcohol): 234 (log ε 4.162), 274 (log ε 3.732), 306-310 (log ε 3.870). For 2,3-dimethylchromone, λ_{max} in mμ (in alcohol): 225 (log ε 4.3885), 268 (log ε 3.8160), 399-304 (log ε 3.9368) [15].

6-Bromochromone-2-carboxylic acid (IX). To the ethylate (from 0.46 g of sodium in 20 ml of anhydrous alcohol) was added a solution of 4.3 g of 2-hydroxy-5-bromoacetophenone and 4.4 g of diethyl oxalate in 2 ml of alcohol. The mixture was heated for two hours at 60-70° and for 2.5 hours with boiling. After cooling we added 17.5 ml of concentrated hydrochloric acid, boiled for 30 minutes, cooled, filtered the precipitate, and washed with bicarbonate. We obtained 3.62 g (61%) of ethyl ester of acid (IX), m.p. 143.5-144° (from alcohol).

Found %: C 48.50; H 3.17; Br 27.15. $C_{12}H_9O_4Br$. Calculated %: C 48.51; H 3.05; Br 26.90.

From the bicarbonate wash solution we precipitated 0.5 g (9%) of acid (IX).

A mixture of 2.97 g of ester, 15 ml of glacial acetic acid, and 7.5 ml of concentrated hydrochloric acid was heated at about 100° for 4 hours, cooled, the precipitate was filtered off, washed with chloroform, and dried at 130°. We obtained 2.62 g (97%) of acid (IX). M.p. 255° (decomposition, from alcohol).

Found %: C 44.59; H 2.01; Br 29.73. $C_{10}H_5O_4Br$. Calculated %: C 44.63; H 1.87; Br 29.70.

Substituted 4-chlorocoumarins. The reaction conditions and characteristics of the substances are given in Table 2. After the end of heating the thionyl chloride or phosphorus oxychloride was distilled off in a vacuum. To the residue we added water and excess sodium bicarbonate (in the case of 6-nitro- and 6,8-dibromo derivatives we used a larger amount of water for solution of the salt of the starting substituted chromonecarboxylic acid). After 4-16 hours (longer decomposition was needed for compounds with electronegative groups) we extracted the corresponding 4-chlorocoumarin with benzene and isolated it by removal of the solvent.

In Table 2 the yields are shown for the sufficiently pure substances. The crude 4-chlorocoumarins (I, VII, VIII) have a satisfactory melting point; the others (II-VI) (yield of crude products respectively 77, 76, 70, 81, and 86%) were purified by treatment with alcohol.

7-Methoxycoumarin. We boiled 0.1 g of 4-chloro-7-methoxycoumarin, 2 ml of acetic acid, 1.5 ml of water, and 1 ml of alcohol with zinc dust for six hours and isolated 0.30 g of 7-methoxycoumarin, recrystallized from ligroin, m.p. 118-119°. According to [17], m.p. 117-118°.

SUMMARY

1. We have obtained a series of substituted 4-chlorocoumarins from the corresponding 2-chromonecarboxylic acids by the action of thionyl chloride or phosphorus pentachloride followed by water decomposition of the intermediate product of the reaction, the acid chloride of the substituted 4,4-dichloro-2-chromonecarboxylic acid.

2. In the case of the unsubstituted intermediate reaction product, 4,4-dichloro-2-chromonedicarboxylic acid (A), it was shown that the direction of splitting of this trichloride under the action of water depends on the acidity of the medium. Increasing acidity of the medium permits increased yield of chromonecarboxylic acid and decreased yield of 4-chlorocoumarin.

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All abbreviations of periodicals in the above bibliography are letter-by-letter transliterations of the abbreviations as given in the original Russian journal. *Some or all of this periodical literature may well be available in English translation.* A complete list of the cover-to-cover English translations appears at the back of this issue.

ORGANIC BORON COMPOUNDS

LXVII.* REACTIONS OF TRIALKYLBORONS WITH ORGANIC ACIDS

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As was shown previously [1] in the action on trialkylborons of compounds with mobile hydrogen (water, alcohols, phenols, amines, mercaptans, thiophenols) there are formed compounds of type (I), and also saturated and unsaturated hydrocarbons and hydrogen.

$$R_3B + HYR' \longrightarrow \underset{(I)}{R_2BYR'} + RH + R_{-H} + H_2$$

Y = O, NH. S; R' = H or a hydrocarbon radical

The temperature at which these reactions begin and the ratio of gaseous products formed are chiefly determined by the nature of the compounds with the mobile hydrogen and to a lesser extent by the size and structure of the hydrocarbon radical in the trialkylborons. With water, alcohols, and amines, the trialkylborons react at 160-200°, forming along the dialkylboric acids, their esters, or N-substituted dialkylboron amines, chiefly olefin hydrocarbons and hydrogen. With mercaptans the reactionbegins at room temperature and is accompanied by formation of esters of dialkylthioboric acid and chiefly (or entirely) saturated hydrocarbons.

In this connection it is interesting to study the reaction of trialkylborons under the influence of organic acids.

The reaction of trialkylboron compounds with organic acids until now has been studied in only one case, by Meerwein and Sönke [2] who by the action of acetic acid on triethylboron obtained diethylboroacetic anhydride (II) and ethane.

$$(C_2H_5)_3B + CH_3COOH \longrightarrow \underset{(II)}{(C_2H_5)_2BOCOCH_3} + C_2H_6$$

In the course of the investigation we repeated the experiments of the above authors and found, in agreement with their results, that the reaction of equimolecular amounts of triethylboron and glacial acetic acid gave as the chief reaction product diethylboroacetic anhydride (II). In the case of reaction of two equivalents of acetic acid on triethylboron, the monoacetate first formed (II) underwent further reaction into ethylpyroboroacetic anhydride (IV). The formation of the latter is explained by the fact that the monoacetate (II) is converted with evolution of ethane into ethylboroacetic anhydride (III), two molecules of which then split out a molecule of acetic anhydride.

$$2\underset{(II)}{(C_2H_5)_2BOCOCH_3} + 2CH_3COOH \longrightarrow 2(C_2H_5)_2BOCOCH_3 \longrightarrow$$

$$\longrightarrow 2C_2H_5B(OCOCH_3)_2 + 2C_2H_6$$

$$\underset{(III)}{\vert}$$

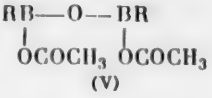
$$C_2H_5B(OCOCH_3)-O-B(OCOCH_3)C_2H_5 + (CH_3CO)_2O$$

$$\underset{(IV)}{}$$

* Communication LXVI, see Izvest. Akad. Nauk SSSR, Otdel Khim. Nauk 2247 (1960).

The resulting mixed anhydrides of pyroboron organic and organic acids were prepared previously by one of us, N. S. Fedotov, and T. A. Shchegoleva by the action of organic acids on phenylboron dichloride, p-chlorophenylboron dichloride, diphenyl boron diphenylboroacetic anhydride [3], esters of n-propylchloroboric acid [4], and also by the action of acetic anhydride on alkyl boric acid or its esters [4, 5].

In the same way as with boron triethyl, higher trialkylborons (tri-n-butyl boron and tri-isobutyl boron) began to react with acetic acid at room temperature and the temperature rose spontaneously to 50-60°. For completion of the process the reaction mass was heated for a short time at 60-100°. In distinction from the triethyl boron, the higher trialkyl borons reacted in any ratio with acetic acid with formation of the corresponding alkylpyroboroacetic anhydrides. When the reaction was carried out with excess acetic acid, the process was ended after separation of two moles of saturated hydrocarbon and when the reaction mixture was distilled we obtained good yields of n-butylpyroboroacetic anhydride (V, R = n-C_4H_9) or isobutylpyroboroacetic anhydride (V, R = iso-C_4H_9), which had been obtained previously by one of us and T. A. Shchegoleva from alkylboric acid [4, 5].

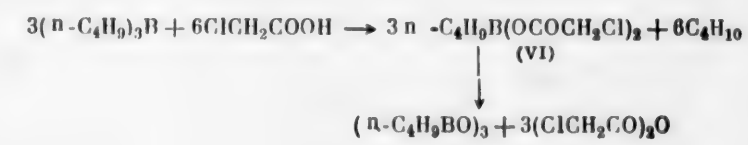


(V)

R = n-C_4H_9, iso-C_4H_9.

In those experiments where the amount of acetic acid did not reach two equivalents per equivalent of starting trialkylboron, part of the trialkylboron compound always remained unchanged and was separated in the distillation of the products of the reaction along with the corresponding alkylpyroboroacetic anhydride.

We also studied the reaction between tri-n-butylboron and monochloroacetic acid. The latter also reacted rather energetically with the trialkylboron, and as in the experiments with acetic acid, for two equivalents of acids and one equivalent of starting trialkylboron compound, two equivalents of butane were evolved. In this case the reaction product was not the expected n-butylpyroborochloroacetic anhydride, but the anhydrides of n-butylboric and chloroacetic acids which probably were formed as a result of splitting of the originally formed n-butylborochloroacetic anhydride (VI).



EXPERIMENTAL

The reaction of the acids with the trialkylborons was carried out in an apparatus consisting of a three-necked flask fitted with a thermometer and dropping funnel, and connected through a reflux condenser with a graduated gasometer. All the operations were carried out in an atmosphere of dry nitrogen.

n-Butylpyroboroacetic Anhydride

a) Reaction of tri-n-butylboron with acetic acid (1 : 1). To 6.52 g (0.036 g mole) of tri-n-butylboron was added without cooling 2.15 g (0.036 g mole) of glacial acetic acid. The mixture warmed to 50° and in the first ten minutes evolved 400 ml of gas. The reaction mixture was heated for one hour at 60-70°, after which the volume of gas reached 850 ml and gas formation practically stopped. The apparatus was cooled and 400 ml of dry nitrogen was passed through. In the gas mixture we found 0.032 g mole of butane and also traces of butylene and hydrogen. The mixture of liquid reaction products was distilled in a vacuum. We separated 3.1 g of tri-n-butylboron with b.p. 85-90° (10 mm) and 2.4 g of n-butylpyroboroacetic anhydride with b.p. 142-144° (10 mm); m.p. 53-57°.

b) Reaction of tri-n-butylboron with acetic acid (1 : 2). To 7.98 g (0.044 g mole) of tri-n-butylboron was added 5.76 g (0.096 g mole) of acetic acid. The reaction was accompanied by energetic gas formation and heating. After heating the mixture for one hour at 100° the volume of gas in the gasometer was 1800 ml. In the gas mixture we found 0.066 g mole of butane, and distillation of the liquid products gave 5.32 g (89.6 %) of n-butylpyroboroacetic anhydride with b.p. 142-144° (10 mm), m.p. 53-57°.

Isobutylpyroboroacetic anhydride. In the reaction we took 8.90 g (0.049 g mole) of triisobutylboron and 6.29 g (0.104 g mole) of glacial acetic acid. As a result of heating the mixture for one hour at 100° we obtained 5.20 g

(78.7%) of pyroacetate of isobutyl boric acid with b.p. 129-131° (10 mm) and m.p. 42-45°, and 0.085 g mole of isobutane. The mixture of gaseous reaction products contained only a trace of isobutylene and hydrogen.

Ethylpyroboroacetic anhydride. To 9.06 g (0.092 g mole) of freshly distilled triethylboron we added dropwise without cooling 11.4 g (0.18 g mole) of glacial acetic acid. The first half of the acid reacted very energetically. The temperature of the mixture quickly rose to 90-95° and the volume of gas in the gasometer reached 2700 ml. The contents of the flask set to a colorless crystalline mass. The second half of the acetic acid reacted less strongly, but evolution of ethane continued. The solid acetate dissolved somewhat in the acid and the volume of gas after heating for one hour reached 5500 ml. In the gaseous reaction products we found 0.164 g mole of ethane. The liquid product was distilled in a vacuum. We separated 6.40 g (65%) of ethylpyroboroacetic anhydride with b.p. 126-127° (25 mm).

Found %: C 44.44, 44.72; H 7.40, 7.50; B 9.71, 9.84. $C_8H_{16}O_5B_2$. Calculated %: C 44.93; H 7.54; B 10.12.

The pyroacetate consisted of colorless needle shaped crystals, soluble in alcohol, ether, benzene.

Reaction between tri-n-butylboron and monochloroacetic acid. To 10.50 g (0.058 g mole) of tri-n-butylboron was added a solution of 11.04 g (0.116 g mole) of monochloroacetic acid in 15 ml of benzene. The reaction solution was heated at 50-70° until evolution of gas stopped. The final volume of gas in the gasometer was 3000 ml. After cooling, 500 ml of dry nitrogen was passed through the apparatus. In the mixture of gaseous reaction products we found 0.107 g mole of butane. The benzene was distilled from the reaction product in a vacuum and the residue was kept at 100° (10 mm), then cooled and treated with isopentane. The colorless crystalline precipitate was filtered off, washed with cooled isopentane, and dried in a vacuum. We obtained 4.69 g of anhydride of monochloroacetic acid with m.p. 43-47°. The isopentane filtrate was evaporated and the residue was distilled in a vacuum. We isolated 3.94 g (68%) of anhydride of n-butyl boric acid with b.p. 97-98° (3 mm), n_D^{20} 1.4241.

Found %: B 12.28, 12.01. C_4H_9OB. Calculated %: B 12.89.

SUMMARY

1. In the reaction of equimolecular amounts of triethylboron and acetic acid we obtain diethylboroacetic anhydride and ethane. At a mole ratio of these reagents of 1 : 2, ethylpyroboroacetic anhydride and ethane are formed.

2. In the reaction of tri-n-butylboron or triisobutylboron and acetic acid in any ratios, the corresponding alkylpyroboroacetic anhydrides and n-butane or isobutane are formed.

3. In the action of chloroacetic acid on tri-n-butylboron the anhydrides of n-butyl boric and chloroacetic acids are formed with n-butane.

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ORGANIC BORON COMPOUNDS

LXVIII. DIALKYLBOROAMINES AND THEIR N-SUBSTITUENTS

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By the action of ammonia on the n-butyl ester of di-n-butylthioboricacid (150°) we obtained di-n-butylboroamine [1]. We later synthesized this amine and also diisoamylboroamine from the corresponding trialkyl borons and ammonia in the presence of n-butylmercaptan which played the role of a catalyst for the process of substitution of one alkyl radical on the boron atom by the amino group [2].

The present communication is devoted to the synthesis of a series of dialkylboroamines and their N-derivatives from esters of dialkylthioboric acids, and also to a study of some properties of the dialkylboroamines.

Esters of dialkylthioboric acids react with ammonia with strong spontaneous heating at room temperature and even with cooling. At the beginning there is formed a crystalline complex compound $R_2BSR' \cdot NH_3$ (I) which at about 20° decomposes with splitting out of a mercaptan and formation of the dialkylboroamine (II).

$$R_2BSR' + NH_3 \longrightarrow R_2B\begin{matrix}SR'\\ \nwarrow\\ NH_3\end{matrix} \longrightarrow R_2BNH_2 + R'SH$$

(I) (II)

$R = C_2H_5$, n-C_3H_7, n-C_4H_9, iso-C_5H_{11}; $R' = C_2H_5$, n-C_3H_7, n-C_4H_9.

Attempts to isolate complex (I) in the pure form under normal conditions did not succeed, although there was no doubt of its formation. Isolation of the complex was complicated by the fact that in the precipitate there could be ammonium mercaptide $RSNH_4$, the possibility of its forming from mercaptan and ammonia at low temperatures was shown by us in special experiments.

Our suggested method for the synthesis of higher dialkylboroamines from trialkyl borons and ammonia in the presence of mercaptans [2] and also by the reaction of ammonia with esters of dialkylthioboric acids at room temperature is simpler as a preparative method because of the greater availability of the starting compounds.

The first member of the series of dialkylboroamines, dimethylboroamine, was obtained by Wiberg and coworkers [3, 4] by heating trimethyl boron with ammonia at 280° and a pressure of 20 atm. This compound was also synthesized by reaction of dimethyl boron chloride with ammonia [5]. Booth and Kraus [6] by the action of ammonia on di-n-butyl boron chloride in the presence of sodium produced a substance with b.p. 100° (0.01 mm) to which they assigned the structure of di-n-butylboroamine. The di-n-butylboroamine which we synthesized earlier [1] had a much lower boiling point (55.5° at 11 mm) and a study of the chemical transformations of the dialkylboroamines clearly showed that they had the structure R_2BNH_2. It is certain that Booth and Kraus obtained some other compound which they erroneously called di-n-butylboroamine. Evers et al. [7] in the reaction of ammonia with di-n-butyl boron cyanide in the presence of sodium obtained a nonvolatile liquid with m.p. -78° which was taken as a polymer of $(n\text{-}C_4H_9)_2BNH_2$.

Thus, there is certain knowledge only of the first member of the series of dialkylboroamines, dimethylboroamine, which exists as a dimer (III).

$$(CH_3)_2B\begin{matrix}NH_2\\ \nwarrow\quad\nearrow\\ NH_2\end{matrix}B(CH_3)_2$$

(III)

with m.p. 9° [3, 4, 5, 8]. In distinction from (III), the higher dialkylboroamines do not solidify even when cooled to -70°, and the measurement of molecular weight (by cryoscopy in benzene) shows that they are monomers.

The dialkylboroamines are very reactive compounds. They are inflammible in air, they are easily hydrolyzed and react with alcohols. Here there is first formed a crystalline ammoniated ester of dialkyl boric acid (IV) which is stable at room temperature but dissociates in a vacuum and when dissolved in isopentane. Thus, under the action of n-butyl alcohol on di-n-butylboroamine we obtain the n-butyl ester of di-n-butyl boric acid (V).

$$(n\text{-}C_4H_9)_2BNH_2 + n\text{-}C_4H_9OH \longrightarrow$$

$$\longrightarrow (n\text{-}C_4H_9)_2B\begin{matrix}\diagup OC_4H_9\text{-}n \\ \diagdown NH_3\end{matrix} \longrightarrow (n\text{-}C_4H_9)_2BOC_4H_9\text{-}n + NH_3$$

(IV) (V)

For the easy dissociation in a vacuum of the complex of ammonia with methyl and ethyl esters of di-n-butyl boric acid, see [9].

Dialkylboroamine ammonia salts are not formed with alkyl halides. Here small amounts of a precipitate separate, with a structure which has not been studied. Dialkylboroamines react with substituted amines by transamination, which leads to obtaining N-substituted dialkylboroamines [2].

Just as dialkylboroamines are smoothly obtained by the action of ammonia on esters of dialkylthioboric acid, N-substituted dialkylboroamines can easily be obtained by the action of primary or secondary amines on thioesters R_2BSR' [1]. In this way, by the passage of ethylamine into the n-butyl ester of di-n-butylthioboric acid we synthesized di-n-butylethylamino boron (VI). The reaction is accompanied by strong spontaneous heating.

$$(n\text{-}C_4H_9)_2BSC_4H_9\text{-}n + C_2H_5NH_2 \longrightarrow (n\text{-}C_4H_9)_2BNHC_2H_5 + n\text{-}C_4H_9SH$$

(VI)

The most suitable method for the synthesis of N-substituted dialkylboroamines is the direct reaction of trialkyl borons and amines in the presence of catalytic amounts of mercaptan. Thus, the addition of diethylamine to tri-n-propylboron which contains n-propyl mercaptan gives 92% di-n-propyldiethylamino boron (VIII) [2].

$$(n\text{-}C_3H_7)_3B + n\text{-}C_3H_7SH \longrightarrow (n\text{-}C_3H_7)_2BSC_3H_7\text{-}n + C_3H_8$$

(VII)

$$\downarrow (C_2H_5)_2NH$$

$$n\text{-}C_3H_7SH + (n\text{-}C_3H_7)_2BN(C_2H_5)_2$$

(VIII)

The n-propyl ester of di-n-propylthioboric acid (VII) obtained in the first step of the reaction forms the amine (VIII) under the influence of diethylamine and regenerates the mercaptan which further reacts with tri-n-butylboron.

It is interesting to note that in carrying out this reaction the order of addition of mercaptan and amine to the trialkylboron is important. When tri-n-propylboron is mixed with diethylamine there is formed, with strong spontaneous heating, a complex compound $(n\text{-}C_3H_7)_3B \leftarrow NH(C_2H_5)_2$ which does not react with n-propyl mercaptan. In this case amine (VIII) is not obtained at 90-100° and so the reaction must be carried out in another way. A small amount (about 1/10 equivalent) of mercaptan is added to the trialkyl boron at room temperature. Energetic reaction begins, accompanied by evolution of the saturated hydrocarbon (in this case propane) and formation of the ester of dialkylthioboric acid (VII) and this quickly stops because of exhaustion of the thiol. Then the amine is added to the reaction mass at a rate which maintains the temperature of the mixture at not above 100° from spontaneous heating.

Until now, there have been five methods for synthesis of N-substituted dialkylboroamines. The first method, described by Wiberg and co-workers [3, 10, 11] consists in heating at 280° and a pressure of 20 atm of trimethyl- or triethylboron with a monosubstituted amine (methylamine, aniline) or a dialkylamine (dimethylamine, diethylamine), which leads to the formation of the corresponding dimethyl or diethylboroamine. Heating trimethylboron with pyrrole gives N-dimethylboropyrrole [13]. As we showed with Vaver [14], the higher trialkyl borons react with

amines at 150-200° and in this case the reaction is accompanied by evolution of a mixture of saturated and unsaturated hydrocarbons and hydrogen and formation of the corresponding N-substituted dialkylboroamines. We found [1] a second satisfactory method for the synthesis of compounds of the type $R_2BNR'_2$ which is that under the action of amines, esters of dialkylthioboric acid split out mercaptans and are converted into nitrogen-containing organic boron compounds. The starting thioester R_2BSR was obtained with great ease and in good yield by reaction of the mercaptan and trialkyl boron [14]. The method of synthesis of dimethyldimethylamino boron from bis(dimethylamino)boron chloride and dimethyl zinc is only of theoretical significance [15]. The fourth and fifth methods were suggested by Burg and Banus [12]. By the action of dimethylamine on tetramethyl diborane they synthesized dimethyldimethylamino boron. They also obtained this compound by reaction of dimethylamine and dimethyl boron chloride. Booth and Kraus reported [6] that in the reaction of ethylamine and di-n-butylboron chloride in the presence of lithium they would obtain di-n-butylethylamino boron (b.p. 100° at 0.02 mm). However, the authors actually did not obtain this compound. The di-n-butylethylamino boron which we obtained had a b.p. 74° (8 mm).

EXPERIMENTAL *

Diethylboroamine. Ammonia was passed into the ethyl ester of diethylthioboric acid (8.6 g) placed in a Favorskii flask and cooled to -70°; the crystalline precipitate of the complex compound formed and by standing at room temperature for 15 hours was spontaneously converted into the diethylboroamine and ethyl mercaptan. Distillation of the reaction product gave 5 g (88.9%) of diethylboroamine with b.p. 72-73°, n_D^{20} 1.4210; d_4^{20} 0.7427.

Found %: C 56.76, 56.92; H 14.19, 14.11; B 12.55. $C_4H_{12}BN$. Calculated %: C 56.54; H 14.24; B 12.73.

Diethylboroamine was a mobile, colorless liquid with a sharp specific odor, inflammible in air.

Di-n-propylboroamine. a) We placed in a Favorskii flask 48.2 g of ethyl ester of di-n-propylthioboric acid and passed in ammonia for 15 minutes. At first a white, crystalline precipitate appeared and then quickly vanished, accompanied by very strong heating of the reaction mass. Then, without stopping passing of ammonia, the mixture was heated to 80°. We separated 20 ml (98.2%) of ethyl mercaptan. The residue was fractionated in a vacuum. We obtained 31.2 g (98.5%) of di-n-propylboroamine with b.p. 65-68° (110 mm). After repeated redistillations the substance had b.p. 64-65° (96 mm), n_D^{20} 1.4170, d_4^{20} 0.7480.

Found %: C 63.92, 63.80; H 14.36, 14.17; B 9.66, 9.27. $C_6H_{16}BN$. Calculated %: C 63.76; H 14.27; B 9.57.

Di-n-propylboroamine was a colorless liquid with a sharp odor. Soluble in organic solvents. It inflamed in air.

b) In the course of 25 minutes ammonia was passed into the n-butyl ester of di-n-propylthioboric acid (22.1 g) heated to 95-100° (bath temperature). After two fractionations of the reaction product we obtained 7.4 g of di-n-propylboroamine with b.p. 123-125°.

c) In a two-necked flask with a reflux condenser was placed a solution of 10.58 g of n-propyl ester of di-n-propyl thioboric acid in 15 ml of isopentane, the mixture was cooled with dry ice in acetone, and dry ammonia was passed in for 15 minutes. The white, crystalline precipitate of complex compound was filtered under nitrogen and washed with isopentane. After keeping in a vacuum, the complex was fully decomposed with formation of a liquid product consisting of n-propyl mercaptan and di-n-propylboroamine. By fractionation we obtained 5.8 g (73%) of di-n-propylboroamine with b.p. 66-68° (110 mm).

Di-n-butylboroamine. To 20.77 g of tri-n-butylboron was added 10 ml of ethyl mercaptan and the mixture was heated to boiling for 15 minutes. Ammonia was passed into the reaction mixture for 25 minutes. The white precipitate which separated quickly changed into a liquid. After fractionation of the reaction mixture we obtained 14.19 g (88.5%) of di-n-butylboroamine with b.p. 64-66° (17 mm), n_D^{20} 1.4277. We previously obtained this compound by reaction of the n-butyl ester of di-n-butylthioboric acid and ammonia with a b.p. of 55-56° (11 mm), n_D^{20} 1.4278 [1].

Diisoamylboroamine. In a Favorskii flask fitted with a dropping funnel we placed 50.3 g of triisoamylboron and 12 ml of ethyl mercaptan was added. The isopentane which formed was distilled off and the residue was heated to 100° and 8 ml more of ethyl mercaptan was added dropwise. The mixture was heated to boiling for 10 minutes and then the cooled reaction mass was treated with ammonia. At first a precipitate of the complex compound appeared, and after further passing of ammonia this vanished while a very strong heating of the reaction mass occurred.

* Still operation conducted in an atmosphere of nitrogen.

On distillation of the reaction product we obtained 28.7 g of diisoamylboroamine with b.p. 72-75° (10 mm); the yield was 75.7% based on the triisoamylboron used in the reaction. After repeated distillations the substance had b.p. 74-75° (10 mm), n_D^{20} 1.4298. This compound was previously obtained by us and had the same constants [2].

Reaction of n-butyl ester of di-n-butylthioboric acid with ethylamine. Di-n-butylethylaminoboron. In a two-necked flask with a descending condenser we placed 12.3 g of n-butyl ester of di-n-butylthioboric acid and passed in ethylamine for 15 minutes. Strong spontaneous heating of the reaction mixture occurred. By vacuum fractionation we obtained 9.2 g (94.7%) of di-n-butylethylaminoboron with b.p. 87-90° (16 mm). After repeated distillations the substance had b.p. 73-74° (8 mm), n_D^{20} 1.4279, d_4^{20} 0.7682.

Found %: C 70.62, 70.56; H 14.33, 14.27; B 6.57, 6.61. $C_{10}H_{24}BN$. Calculated %: C 71.01; H 14.30; B 6.40.

Di-n-butylethylaminoboron was a colorless, mobile liquid. It was stable in nitrogen atmosphere. In air it oxidized and hydrolyzed. It was soluble in organic solvents.

Reaction of di-n-butylboroamine with n-butyl alcohol. To 5.96 g of di-n-butylboroamine we added dropwise 4 ml of n-butyl alcohol. A white, crystalline precipitate appeared which did not split by standing for 15 days. When isopentane was added to the precipitate, and also by keeping it in a vacuum there was decomposition of the ammonia complex of the n-butyl ester of di-n-butylboric acid with evolution of ammonia. After vacuum fractionation we obtained 7.58 g (90.6%) of n-butyl ester of di-n-butylboric acid with b.p. 88-89.5° (6 mm), n_D^{20} 1.4216. The literature values are b.p. 92-94° (8 mm), n_D^{20} 1.4222 [14].

SUMMARY

1. Esters of dialkylthioboric acids at room temperature react with ammonia and amines with formation of dialkylboroamines and their N-substituted derivatives.

2. Dialkylboroamines and their N-derivatives are easily obtained by reaction of trialkyl borons and ammonia or amines in the presence of mercaptans.

3. In the reaction with alcohols dialkylboroamines are converted into esters of dialkylboric acids.

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ARYL ESTERS OF N-DIARYLOXYPHOSPHINYLIMINOTHIOCARBOXYLIC ACIDS OF THE AROMATIC SERIES

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In a previous communication [1] we described the preparation of diesters of thioacylamidophosphoric acid.

$$ArC[=NPO(OR)_2]Cl + H_2S \xrightarrow{+(C_2H_5)_3N} ArC(=S)NHPO(OR)_2$$

These diesters are tautomeric with N-diaryloxyphosphinyliminothiocarboxylic acids.

$$ArC(=S)NHPO(OR)_2 \rightleftarrows ArC[=NPO(OR)_2]SH.$$

Aromatic esters of N-diaryloxyphosphinyliminothiocarboxylic acids (I) can be obtained by reaction of the acid chlorides of N-diaryloxyphosphinyliminocarboxylic acids [2] with sodium thiophenolates in the presence of tertiary amines.

$$ArC[=NPO(OAr')_2]Cl \xrightarrow[\text{or } NaSAr'']{+HSAr''+(C_2H_5)_3N} ArC[=NPO(OAr')_2]SAr''$$

With thiophenols in the presence of tertiary amines in benzene or dioxane solution the reaction takes place very easily with evolution of heat and is completed by heating the mixture to boiling. Sodium thiophenolate reacts with more difficulty and to complete the reaction the mixture must be boiled for 1-3 hours, and the yield in most cases is 10-15% lower than in the first case.

The esters (I) are colorless or slightly yellow (nitrosubstituted) crystalline substances of neutral character, insoluble in water, alkali, or acid (Table 1). Phenyl and p-nitrophenyl esters of N-diaryloxyphosphinyliminothiocarboxylic acids which do not contain nitro groups distil in a high vacuum without decomposition. p-Nitrophenyl esters of N-diaryloxyphosphinyliminothiocarboxylic acids when heated in a high vacuum gradually decompose (250-300°) with formation of the corresponding nitriles and considerable carbonization. Triarylmonothiolphosphates could not be isolated from the reaction mixture.

In chemical properties the esters (I) are very similar to aryl esters of N-diaryloxyphosphinyliminocarboxylic acids [3]. Just like these, (I) are not saponified by boiling with a water solution of alkali hydroxide, which is explained by their slight solubility in water, but are easily saponified by heating with a water-alcohol solution of alkali with formation of salts of diesters of acylamidophosphoric acids and thiophenols.

$$ArC[=NPO(OAr')_2]SAr'' + OH^- \longrightarrow Ar''SH + [ArCONPO(OAr')_2]^-$$

Compounds (I) are easily saponified by water-alcohol solutions of strong mineral acids and also by 90% acetic acid. By the action of ammonia or amines on (I) the thioaryloxyl group is replaced by the amino group with formation of the corresponding amides (Table 2) and thiophenols.

$$ArC[=NPO(OAr')_2]SAr'' + RNH_2 \longrightarrow Ar''SH + ArC[=NPO(OAr')_2]NHR$$

TABLE 1. Esters of N-Diaryloxyphosphinyliminothiocarboxylic Acids of the Type

Ar	Ar'	Ar"	Method of preparation*	Yield, %	M.p.	Appearance; from what crystallized
C_6H_5	C_6H_5	C_6H_5	A	95	104—105°	Prisms, benzene, alcohol
			B	81		
C_6H_5	C_6H_5	p-ClC_6H_4	A	96	122—123	Prisms, alcohol, benzene
			B	80		
C_6H_5	C_6H_5	p-$NO_2C_6H_4$	A	95	133—134	Prisms, alcohol, dioxane
			C	87		
C_6H_5	p-ClC_6H_4	C_6H_5	A	68	142—143	Prisms, alcohol, dioxane
C_6H_5	p-ClC_6H_4	p-ClC_6H_4	A	69	169—170	Platelets, alcohol + dioxane
C_6H_5	p-ClC_6H_4	p-$NO_2C_6H_4$	C	75	177—178	Prisms, dioxane
C_6H_5	p-$NO_2C_6H_4$	C_6H_5	A	97	179—180	Prisms, alcohol + dioxane
C_6H_5	p-$NO_2C_6H_4$	p-ClC_6H_4	A	94	192—193	Needles, dioxane
C_6H_5	p-$NO_2C_6H_4$	p-$NO_2C_6H_4$	C	90	184—185	Prisms, dioxane
C_6H_5	α-$C_{10}H_7$	C_6H_5	A	63	83—84	Prisms, alcohol
C_6H_5	α-$C_{10}H_7$	p-ClC_6H_4	A	88	126—127	Needles, dioxane
C_6H_5	α-$C_{10}H_7$	p-$NO_2C_6H_4$	C	76	160—161	Prisms, dioxane
o-$NO_2C_6H_4$	C_6H_5	C_6H_5	A	90	150—151	Prisms, alcohol + dioxane
o-$NO_2C_6H_4$	C_6H_5	p-ClC_6H_4	A	93	121—122	Prisms, alcohol
o-$NO_2C_6H_4$	C_6H_5	p-$NO_2C_6H_4$	C	73	114—115	Prisms, alcohol
o-$NO_2C_6H_4$	p-ClC_6H_4	C_6H_5	A	73	128—129	Prisms, alcohol
o-$NO_2C_6H_4$	p-ClC_6H_4	p-ClC_6H_4	A	77	135—136	Prisms, benzene, alcohol
o-$NO_2C_6H_4$	p-ClC_6H_4	p-$NO_2C_6H_4$	C	84	154—155	Prisms, benzene
o-$NO_2C_6H_4$	p-$NO_2C_6H_4$	C_6H_5	A	95	172—173	Prisms, dioxane
o-$NO_2C_6H_4$	p-$NO_2C_6H_4$	p-ClC_6H_4	A	94	183—184	Clumps of needles, dioxane
o-$NO_2C_6H_4$	p-$NO_2C_6H_4$	p-$NO_2C_6H_4$	C	87	169—170	Prisms, dioxane
m-$NO_2C_6H_4$	C_6H_5	C_6H_5	A	89	89—90	Needles, alcohol
m-$NO_2C_6H_4$	C_6H_5	p-ClC_6H_4	A	84	119—120	Clumps of needles, benzene
m-$NO_2C_6H_4$	C_6H_5	p-$NO_2C_6H_4$	C	74	157—158	Needles, dioxane

* See experimental part.

** None of the compounds dissolved in water or ligroin at the boiling point. ‡ Easily soluble at 20°. + easily soluble at the boiling point, −difficultly soluble at the boiling point, = not soluble at the boiling point.

ArC [= NPO(OAr')$_2$]SAr''

Formula	Found, %	Calculated, %	Solvent**					
			Ether	CCl_4	C_6H_6	Alcohol	Acetone	Dioxane
$C_{25}H_{20}O_3NSP$	N 3.25, 3.40; S 7.02, 7.15; P 6.89, 6.97	N 3.14, S 7.20; P 6.95	−	−	+	+	±	±
$C_{25}H_{19}O_3NSClP$	Cl 7.33, 7.46	Cl 7.39	−	−	+	+	±	±
$C_{25}H_{19}O_5N_2SP$	N 5.67, 5.84	N 5.71	=	=	+	+	±	±
$C_{25}H_{18}O_3NSCl_2P$	Cl 13.41, 13.47	Cl 13.79	=	=	+	−	±	±
$C_{25}H_{17}O_3NSCl_3P$	Cl 19.18, 19.42; P 5.71	Cl 19.38; P 5.64	=	=	−	−	+	+
$C_{25}H_{17}O_5N_2SCl_2P$	N 4.97, 5.08; Cl 12.67; 12.69	N 5.01, Cl 12.68	=	=	−	−	+	+
$C_{25}H_{18}O_7N_3SP$	N 7.92, 8.01	N 7.85	=	=	−	−	+	+
$C_{25}H_{17}O_7N_3SClP$	N 7.48, 7.55	N 7.37	=	=	−	−	+	+
$C_{25}H_{17}O_9N_4SP$	N 9.42, 9.60	N 9.65	=	=	−	−	+	+
$C_{33}H_{24}O_3NSP$	N 2.49, 2.52	N 2.57	−	−	±	+	±	±
$C_{33}H_{23}O_3NSClP$	N 2.34, 2.43; Cl 6.23, 6.37	N 2.42; Cl 6.11	=	−	+	+	±	±
$C_{33}H_{23}O_5N_2SP$	N 4.73, 4.83	N 4.74	=	=	−	−	+	+
$C_{25}H_{19}O_5N_2SP$	N 5.66, 5.79	N 5.71	=	=	+	−	+	+
$C_{25}H_{18}O_5N_2SClP$	N 5.48, 5.45	N 5.34	−	−	±	−	±	±
$C_{25}H_{18}O_7N_3SP$	N 8.01, 8.09; S 5.90, 5.93	N 7.85; S 5.99	=	=	−	−	+	+
$C_{25}H_{17}O_5N_2SCl_2P$	N 5.18. 5.21; Cl 12.44, 12.60	N 5.01; Cl 12.68	−	−	+	+	±	±
$C_{25}H_{16}O_5N_2SCl_3P$	Cl 17.91, 17.98	Cl 17.91	−	=	+	+	±	±
$C_{25}H_{16}O_7N_3SCl_2P$	Cl 11.78, 11.93	Cl 11.73	=	=	+	−	±	±
$C_{25}H_{17}O_9N_4SP$	N 9.54, 9.72	N 9.65	=	=	−	−	+	+
$C_{25}H_{16}O_9N_4SClP$	Cl 5.81, 5.85	Cl 5.77	=	=	−	−	+	+
$C_{25}H_{16}O_{11}N_5SP$	N 11.17; 11.18	N 11.20	=	=	−	−	+	+
$C_{25}H_{19}O_5N_2SP$	N 5.81, 5.86	N 5.71	=	−	+	+	±	±
$C_{25}H_{18}O_5N_2SClP$	N 5.44, 5.53; Cl 6.73, 6.74; P 5.93	N 5.34; Cl 6.75; P 5.90	=	−	+	+	±	±
$C_{25}H_{18}O_7N_3SP$	N 7.90, 7.96	N 7.85	=	=	−	−	+	+

TABLE 1 (continued)

Ar	Ar'	Ar''	Method of preparation	Yield, %	M.p.	Appearance; from what crystallized
m-$NO_2C_6H_4$	p-ClC_6H_4	C_6H_5	A	87	127—128°	Clumps of needles, benzene
m-$NO_2C_6H_4$	p-ClC_6H_4	p-ClC_6H_4	A	88	140—141	Prisms, benzene, alcohol
m-$NO_2C_6H_4$	p-ClC_6H_4	p-$NO_2C_6H_4$	C	80	150—151	Prisms, benzene
m-$NO_2C_6H_4$	p-$NO_2C_6H_4$	C_6H_5	A	90	171—172	Prisms, dioxane
m-$NO_2C_6H_4$	p-$NO_2C_6H_4$	p-ClC_6H_4	A	83	179—180	Prisms, dioxane
m-$NO_2C_6H_4$	p-$NO_2C_6H_4$	p-$NO_2C_6H_4$	C	84	185—186	Prisms, dioxane
p-$NO_2C_6H_4$	C_6H_5	C_6H_5	A	90	116—117	Prisms, benzene
p-$NO_2C_6H_4$	C_6H_5	p-ClC_6H_4	A	90	166—167	Needles, alcohol + + dioxane
p-$NO_2C_6H_4$	C_6H_5	p-$NO_2C_6H_4$	C	89	185—186	Prisms, dioxane
p-$NO_2C_6H_4$	p-ClC_6H_4	C_6H_5	C	80	135—136	Clumps of needles, benzene
p-$NO_2C_6H_4$	p-ClC_6H_4	p-ClC_6H_4	B	81	157—158	Needles, benzene
p-$NO_2C_6H_4$	p-ClC_6H_4	p-$NO_2C_6H_4$	C	95	154—155	Clumps of needles, alcohol + dioxane
p-$NO_2C_6H_4$	p-$NO_2C_6H_4$	C_6H_5	A	84	174—175	Prisms, dioxane
p-$NO_2C_6H_4$	p-$NO_2C_6H_4$	p-ClC_6H_4	B	80	191—192	Prisms, dioxane
p-$NO_2C_6H_4$	p-$NO_2C_6H_4$	p-$NO_2C_6H_4$	C	76	208—209	Needles, dioxane
3,5-$(NO_2)_2C_6H_3$	C_6H_5	C_6H_5	A	92	117—118	Prisms, alcohol
3,5-$(NO_2)_2C_6H_3$	C_6H_5	p-ClC_6H_4	A	97	142—143	Prisms, alcohol + dioxane
3,5-$(NO_2)_2C_6H_3$	C_6H_5	p-$NO_2C_6H_4$	C	95	145—146	Needles, alcohol + + dioxane, benzene
3,5-$(NO_2)_2C_6H_3$	p-ClC_6H_4	C_6H_5	A	86	145—146	Prisms, dioxane
3,5-$(NO_2)_2C_6H_3$	p-ClC_6H_4	p-ClC_6H_4	A	91	165—166	Needles, dioxane
3,5-$(NO_2)_2C_6H_3$	p-ClC_6H_4	p-$NO_2C_6H_4$	C	72	200—201	Prisms, dioxane
3,5-$(NO_2)_2C_6H_3$	p-$NO_2C_6H_4$	C_6H_5	A	80	171—172	Prisms, dioxane
3,5-$(NO_2)_2C_6H_3$	p-$NO_2C_6H_4$	p-ClC_6H_4	A	81	175—176	Prisms, dioxane
p-ClC_6H_4	C_2H_5	C_6H_5	B	73	114—115	Prisms, benzene, alcohol
p-ClC_6H_4	C_6H_5	p-ClC_6H_4	B	89	141—142	Prisms, benzene, alcohol
p-ClC_6H_4	C_6H_5	p-$NO_2C_6H_4$	C	80	168—169	Prisms, dioxane, alcohol
p-ClC_6H_4	p-ClC_6H_4	C_6H_5	B	79	136—137	Clumps of needles, benzene, alcohol
p-ClC_6H_4	p-ClC_6H_4	p-ClC_6H_4	B	82	142—143	Clumps of needles, benzene, alcohol
p-ClC_6H_4	p-ClC_6H_4	p-$NO_2C_6H_4$	C	70	142—143	Clumps of needles, benzene, dioxane

TABLE 1 (continued)

Formula	Found, %	Calculated, %	Solvent**					
			Ether	CCl_4	C_6H_6	Alcohol	Acetone	Dioxane
$C_{25}H_{17}O_5N_2SCl_2P$	N 5.07, 5.09; Cl 12.46, 12.60	N 5.01; Cl 12.68	=	–	+	+	+ +	+ +
$C_{25}H_{16}O_5N_2SCl_3P$	Cl 18.07, 18.13	Cl 17.91	=	=	+	–	+	+
$C_{25}H_{16}O_7N_3SCl_2P$	Cl 11.60, 11.61	Cl 11.73	=	=	+	–	+	+
$C_{25}H_{17}O_9N_4SP$	N 9.50, 9.51	N 9.65	=	=	–	–	+	+
$C_{25}H_{16}O_9N_4SClP$	Cl 5.87, 5.92	Cl 5.77	=	=	–	–	+	+
$C_{25}H_{16}O_{11}N_5SP$	N 10.98, 11.05	N 11.20	=	=	–	–	+	+
$C_{25}H_{19}O_5N_2SP$	N 5.50, 5.62	N 5.71	=	=	+	–	+	+
$C_{25}H_{18}O_5N_2SClP$	N 5.32, 5.42; Cl 6.71, 6.74	N 5.34; Cl 6.75	=	=	+	–	+	+
$C_{25}H_{18}O_7N_3SP$	N 7.63, 7.69	N 7.85	=	=	–	–	+	+
$C_{25}H_{17}O_5N_2SCl_2P$	Cl 12.53, 12.57	Cl 12.68	–	–	+	+	+ +	+ +
$C_{25}H_{16}O_5N_2SCl_3P$	N 4.62, 4.79; Cl 17.95, 18.01	N 4.72; Cl 17.91	–	–	+	+	+ +	+ +
$C_{25}H_{16}O_7N_3SCl_2P$	N 7.03, 7.04	N 6.95	=	=	–	–	+	+
$C_{25}H_{17}O_9N_4SP$	N 9.78, 9.85	N 9.65	=	=	–	–	+	+
$C_{25}H_{16}O_9N_4SClP$	N 9.15, 9.26	N 9.11	=	=	–	–	+	+
$C_{25}H_{16}O_{11}N_5SP$	N 11.08, 11.12	N 11.20	=	=	–	–	+	+
$C_{25}H_{18}O_7N_3SP$	N 7.95, 8.09	N 7.85	=	–	+	+	+ +	+ +
$C_{25}H_{17}O_7N_3SClP$	N 7.36, 7.52; Cl 6.15, 6.28	N 7.37; Cl 6.22	=	=	+	–	+ +	+ +
$C_{25}H_{17}O_9N_4SP$	N 9.63, 9.71	N 9.65	=	=	–	–	+	+ +
$C_{25}H_{16}O_7N_3SCl_2P$	Cl 11.92, 12.00	Cl 11.73	=	=	+	–	+ +	+ +
$C_{25}H_{15}O_7N_3SCl_3P$	Cl 16.57, 16.63	Cl 16.65	=	=	+	–	+	+ +
$C_{25}H_{15}O_9N_4SCl_2P$	Cl 10.63, 10.69	Cl 10.92	=	=	–	–	+	+
$C_{25}H_{16}O_{11}N_5SP$	N 11.29, 11.36	N 11.20	=	=	–	–	+	+
$C_{25}H_{15}O_{11}N_5SClP$	N 10.43, 10.48; Cl 5.35, 5.37	N 10.63; Cl 5.38	=	=	–	–	+	+
$C_{25}H_{19}O_3NSClP$	Cl 7.45, 7.62	Cl 7.39	–	–	+	+	+ +	+ +
$C_{25}H_{18}O_3NSCl_2P$	Cl 13.69, 13.75	Cl 13.79	–	–	+	+	+ +	+ +
$C_{25}H_{18}O_5N_2SClP$	N 5.09, 5.22; Cl 6.62, 6.70	N 5.34; Cl 6.75	=	=	–	–	+	+
$C_{25}H_{17}O_3NSCl_3P$	Cl 19.19, 19.40	Cl 19.38	–	–	+	+	+ +	+ +
$C_{25}H_{16}O_3NSCl_4P$	Cl 24.10, 24.12	Cl 24.32	–	–	+	+	+ +	+ +
$C_{25}H_{16}O_5N_2SCl_3P$	Cl 17.72, 17.74	Cl 17.91	=	=	+	–	+ +	+ +

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TABLE 1 (continued)

Ar	Ar'	Ar"	Method of preparation*	Yield, %	M.p.	Appearance; from what crystallized
p-ClC_6H_4	p-$NO_2C_6H_4$	C_6H_5	A	96	165—166°	Prisms, dioxane
p-ClC_6H_4	p-$NO_2C_6H_4$	p-ClC_6H_4	A	83	177—178	Prisms, dioxane
p-ClC_6H_4	p-$NO_2C_6H_4$	p-$NO_2C_6H_4$	C	78	182—183	Prisms, dioxane
p-BrC_6H_4	C_6H_5	C_6H_5	A	87	109—110	Prisms, benzene, alcohol
p-BrC_6H_4	C_6H_5	p-ClC_6H_4	A	84	140—141	Prisms, benzene, alcohol
p-BrC_6H_4	C_6H_5	p-$NO_2C_6H_4$	C	78	165—166	Prisms, dioxane
α-$C_{10}H_7$	C_6H_5	C_6H_5	A	81	116—117	Clumps of needles, benzene; prisms, alcohol
α-$C_{10}H_7$	C_6H_5	p-ClC_6H_4	A	75	93—94	Prisms, alcohol
α-$C_{10}H_7$	C_6H_5	p-$NO_2C_6H_4$	C	88	101—102	Prisms, benzene, alcohol

TABLE 2. N-Diaryloxyphosphinylarinamidines Obtained by the Scheme: $ArC[=NPO(OAr')_2]SAr'' + RNH_2 \rightarrow ArC[=NPO(OAr')_2]NHR + HSAr''$

Ar	Ar'	Ar"	R	Yield, %	Time of reaction (hours)	Literature reference
C_6H_5	C_6H_5	C_6H_5	H	100	0.2	[6]
C_6H_5	C_6H_5	C_6H_5	$C_6H_5CH_2$	91	18	(*)
C_6H_5	C_6H_5	C_6H_5	C_6H_5	59 **	25	[6]
C_6H_5	C_6H_5	C_6H_5	p-$CH_3C_6H_4$	75	22	(*)
C_6H_5	C_6H_5	C_6H_5	p-ClC_6H_4	48, 86 ***	25	(*)
C_6H_5	C_6H_5	C_6H_5	p-BrC_6H_4	16	25	(*)
C_6H_5	C_6H_5	C_6H_5	p-$NO_2C_6H_4$	4, 86 ***	33	(*)
C_6H_5	C_6H_5	p-ClC_6H_4	H	94	0.2	[6]
C_6H_5	C_6H_5	p-ClC_6H_4	$C_6H_5CH_2$	98	18	(*)
C_6H_5	C_6H_5	p-ClC_6H_4	C_6H_5	65	20	[6]
C_6H_5	C_6H_5	p-$NO_2C_6H_4$	C_6H_5	81	12	[6]
p-ClC_6H_4	C_6H_5	C_6H_5	H	100	0.2	[6]
p-ClC_6H_4	p-ClC_6H_4	C_6H_5	H	98	0.2	[7]
p-BrC_6H_4	C_6H_5	C_6H_5	H	61	0.2	(*)
p-BrC_6H_4	C_6H_5	p-ClC_6H_4	H	70	0.2	(*)
o-$NO_2C_6H_4$	C_6H_5	C_6H_5	H	92	2	(*)
o-$NO_2C_6H_4$	C_6H_5	p-$NO_2C_6H_4$	H	90	0.2	(*)
o-$NO_2C_6H_4$	p-ClC_6H_4	p-ClC_6H_4	H	76	2	(*)
m-$NO_2C_6H_4$	C_6H_5	C_6H_5	H	91	0.2	[6]
m-$NO_2C_6H_4$	p-$NO_2C_6H_4$	p-$NO_2C_6H_4$	H	51, 94 ***	0.1	(*)
p-$NO_2C_6H_4$	C_6H_5	p-$NO_2C_6H_4$	H	81	0.1	[6]
p-$NO_2C_6H_4$	C_6H_5	p-$NO_2C_6H_4$	C_6H_5	83	12	[6]
p-$NO_2C_6H_4$	p-ClC_6H_4	p-$NO_2C_6H_4$	H	83	0.1	[7]
p-$NO_2C_6H_4$	p-$NO_2C_6H_4$	p-$NO_2C_6H_4$	H	48, 91 ***	0.1	(*)
3,5-$(NO_2)_2C_6H_4$	C_6H_5	p-$NO_2C_6H_4$	H	92	0.1	[6]
α-$C_{10}H_7$	C_6H_5	C_6H_5	H	85	1.5	(*)

* Not described in the literature. Analytical data and properties in Table 4.

** When heated for 12 hours, yield 34%.

*** Yield from N-diaryloxyphosphinyliminoacyl chloride.

TABLE 1 (continued)

Formula	Found, %	Calculated, %	Solvent, **					
			Ether	CCl_4	C_6H_6	Alcohol	Acetone	Dioxane
$C_{25}H_{17}O_7N_3SClP$	Cl 6.16, 6.25	Cl 6.22	=	=	+	–	+	+
$C_{25}H_{16}O_7N_3SCl_2P$	Cl 11.90, 12.02	Cl 11.73	=	=	–	–	+	+
$C_{25}H_{16}O_9N_4SClP$	N 9.27, 9.35; Cl 5.55, 5.70	N 9.11; Cl 5.77	=	=	–	–	+	+
$C_{25}H_{19}O_3NSBrP$	Br 15.30, 15.35	Br 15.24	=	=	+	–	+	+
$C_{25}H_{18}O_3NSClBrP$	(Cl + Br) 20.63, 20.76	(Cl + Br) 20.65	=	=	+	–	+	+
$C_{25}H_{18}O_5N_2SBrP$	N 4.72, 4.82; Br 13.98, 14.04	N 4.92; Br 14.04	=	=	–	–	+	+
$C_{29}H_{22}O_3NSP$	S 6.28, 6.32; P 6.04, 6.10	S 6.47; P 6.25	–	–	+	+	+	+
$C_{29}H_{21}O_3NSClP$	Cl 6.83, 6.88; P 5.87, 6.06	Cl 6.69; P 5.85	–	–	+	+	+	+
$C_{29}H_{21}O_5N_2SP$	N 4.96, 5.18; S 6.17, 6.20	N 5.18; S 5.93	=	=	+	+	+	+

TABLE 3. N-Diaryloxyphosphinylarinamidines Obtained by the Scheme $ArC[=NPO(OAr')_2]OAr'' + RNH_2 \rightarrow ArC[=NPO(OAr')_2]NHR + HOAr''$

Ar	Ar'	Ar''	R	Yield, %	Literature reference
C_6H_5	C_6H_5	C_6H_5	H	85	[6]
C_6H_5	C_6H_5	C_6H_5	C_6H_5	48	[6]
p-ClC_6H_4	C_6H_5	p-ClC_6H_4	H	87	[6]
m-$NO_2C_6H_4$	C_6H_5	C_6H_5	H	90	[6]
m-$NO_2C_6H_4$	C_6H_5	p-$NO_2C_6H_4$	H	81	[6]
m-$NO_2C_6H_4$	p-$NO_2C_6H_4$	p-ClC_6H_4	H	67	(*)
p-$NO_2C_6H_4$	C_6H_5	p-$NO_2C_6H_4$	H	85	[6]
p-$NO_2C_6H_4$	p-ClC_6H_4	p-$NO_2C_6H_4$	H	82	[7]
p-$NO_2C_6H_4$	p-$NO_2C_6H_4$	p-ClC_6H_4	H	62	(*)

* Not described in the literature. Analytical data and properties in Table 4.

thiophenolate and the mixture was boiled under reflux until the acid reaction to Congo vanished in a sample treated with water, which took 1-3 hours. Further treatment was as in process B.

Hydrolysis of aryl esters of N-diaryloxyphosphinyliminocarboxylic acids of the aromatic series. A. In water-alcohol solution of sodium hydroxide. A mixture of 0.003 g mole of (I), 4 ml of 1.5 N water solution of sodium hydroxide, and 60 ml of alcohol was boiled under reflux for one hour. The precipitate dissolved and a clear solution formed (in the case of the p-nitrothiophenyl ester, with a red color). The alcohol was distilled off in a vacuum, the residue was dissolved in 30 ml of water, and the solution was acidified with hydrochloric acid to an acid reaction to Congo. The diester precipitated as an oil which quickly crystallized. The crystals were filtered off, washed with water, with alcohol, and were recrystallized. Yield 60-80%.

B. In a water-alcohol solution of hydrogen chloride. A mixture of 0.002 g mole of (I), 0.4 ml of concentrated hydrochloric acid, and 25 ml of alcohol was boiled under reflux for one hour. The precipitate dissolved and a strong odor of thiophenol developed. The solution was evaporated dry in a vacuum, the residue was treated with ether, the precipitate was filtered off and washed with ether. Yield 80-90%.

In alcohol solution the reaction of (I) with ammonia occurs very easily with evolution of heat and with quantitative or almost quantitative yields. Derivatives of o-nitrobenzoic and α-naphthoic acids react with somewhat more difficulty, evidently because of spacial hindrance. In the case of esters of N-di-p-nitrodiphenoxyphosphinyliminothiocarboxylic acid, the reaction is complicated by the fact that in the reaction with ammonia the p-nitrophenoxyl group also takes part, combining with the phosphorus atom. Therefore the yield of the corresponding amide is lowered, and with long passing of ammonia individual products cannot be isolated from the reaction mixture.

The reaction of (I) with amines (Table 2) occurs with considerably more difficulty. In order to obtain the optimum yield we heated the reaction mixture for 10-35 hours. The reaction rate and yield were greater, the higher the basicity of the reacting amine and the higher the acidity of the thiophenol which splits out.

Thus, the reaction is analogous to the reaction of formation of acid amides from acid chlorides or esters of carboxylic acids and amines. The role of a pseudohalide is played by the thiophenol residue which is split out.

For a comparison of the properties of (I) and aryl esters of N-diaryloxyphosphinyliminocarboxylic acids [3] we studied the reaction of the latter with ammonia and amines. We found that in aromatic esters of N-diaryloxyphosphinyliminocarboxylic acids the aryloxyl group bound to the carbon atom is also replaced by the amino group under the action of ammonia or amines, with formation of the corresponding amidines (Table 3) and phenols.

$$ArC[=NPO(OAr')_2]OAr'' + RNH_2 \longrightarrow Ar''OH + ArC[=NPO(OAr')_2]NHR$$

The properties of the undescribed N-diaryloxyphosphinylareneamidines are given in Table 4.

When (I) are boiled in alcohol solution with phenol (20 hours) replacement of the thioaryloxy group by aryloxy does not occur. By the action of 25% hydrogen peroxide in acetic acid solution at 20°, (I) are not changed, but when heated they are hydrolyzed to diesters of acylamidophosphoric acids. Concentrated nitric acid hydrolyzes (I) to diesters. Bromine does not add to (I). Esters (I) are not changed by heating with methyl iodide without a solvent or with dimethyl sulfate in benzene solution up to 100° for 40 hours. When (I) are heated to 100° with dimethyl sulfate without a solvent alkylation on the sulfur atom does not occur but there is a gradual change of the substance with formation of nitriles, thiophenols, diesters of acylamidophosphoric acids, and other products whose structure is not yet established. Thus, the sulfur in (I) has no properties of sulfide sulfur: it does not add halogens, is not oxidized, does not give sulfonyl salts, and hence (I) by structure and properties are esters of N-substituted iminothiocarboxylic acids.

EXPERIMENTAL

Aryl esters of N-diaryloxyphosphinyliminothiocarboxylic acids of the aromatic series (Table 1). General methods of preparation. A. In the presence of tertiary bases. To a solution of 0.01 g mole of N-diaryloxyphosphinyliminoacyl chloride in 50-150 ml of anhydrous benzene or dioxane was added 0.01 g mole of triethylamine or pyridine or dimethylaniline. The reaction mixture grew hot from the heat of reaction and the hydrochloride of the tertiary amine (in the case of triethylamine and pyridine) precipitated. The mixture was heated to boiling, the hydrochloride of the tertiary amine was filtered off, and the solution was evaporated in a vacuum. The residue was a crystalline mass or a thick oil which crystallized when ether was added. The crystals were ground with 20-30 ml of ether, sucked off, washed with ether and crystallized.

When dimethylaniline was used, its hydrochloride did not precipitate. The solution was evaporated dry in a vacuum, the residue was treated with water to remove the dimethylaniline hydrochloride, and the insoluble portion was recrystallized.

B. From thiophenols and metallic sodium. To a solution of 0.011 g mole of thiophenol in 50-150 ml of benzene or dioxane was added 0.01 g atom of finely divided sodium. When the sodium had reacted, we added 0.01 g mole of N-diaryloxyphosphinyliminoacyl chloride. The reaction mixture was heated until the acid reaction to Congo vanished in a sample obtained by adding 1-2 drops of water to a drop of reaction mixture, which usually required 10-15 minutes. Sodium chloride precipitated from the boiling solution, and further treatment was the same as in process A.

C. From previously prepared sodium thiophenolate. To a solution of 0.01 g mole of N-diaryloxyphosphinyliminoacyl chloride in 50-150 ml of dry benzene or dioxane was added 0.011 g mole of carefully ground dry sodium

TABLE 4. N-Diaryloxyphosphinylarenamidines of the Type $ArC[=NPO(OAr')_2]NHR$ *

Ar	Ar'	R	M.p.	Appearance; from what crystallized	Found, % N	Formula	Calculated, % N	Solubility**					
								Ether	CCl_4	C_6H_6	Alcohol	Acetone	Dioxane
C_6H_5	C_6H_5	$C_6H_5CH_2$	137—138°	Prisms, alcohol	6.12, 6.36	$C_{26}H_{23}O_3N_2P$	6.33	=	—	+	+	+ +	+ +
C_6H_5	C_6H_5	p-$CH_3C_6H_4$	184—185	Platelets, alcohol	6.34, 6.44	$C_{26}H_{23}O_3N_2P$	6.33	=	=	=	—	+	+ +
C_6H_5	C_6H_5	p-ClC_6H_4	198—199	Needles, alcohol + dioxane	***	$C_{25}H_{20}O_3N_2ClP$	***	=	=	—	+	+	+ +
C_6H_5	C_6H_5	p-BrC_6H_4	185—186	Prisms, alcohol + dioxane	5.67, 5.73	$C_{25}H_{20}O_3N_2BrP$	5.52	=	=	=	—	+	+ +
C_6H_5	C_6H_5	p-$NO_2C_6H_4$	246—247	Needles, dioxane	8.78, 8.82	$C_{25}H_{20}O_5N_3P$	8.88	=	=	=	—	—	—
p-BrC_6H_4	C_6H_5	H	68—69	Prisms, CCl_4 + ligroin	6.20, 6.27	$C_{19}H_{16}O_3N_2BrP$	6.50	+	+	+ +	+ +	+ +	+ +
o-$NO_2C_6H_4$	C_6H_5	H	122—123	Prisms, alcohol	10.53, 10.70	$C_{19}H_{16}O_5N_3P$	10.58	=	=	—	—	+ +	+ +
o-$NO_2C_6H_4$	p-ClC_6H_4	H	130—131	Prisms, water + alcohol (1 : 1)	8.90, 9.04	$C_{19}H_{14}O_5N_3Cl_2P$	9.01	—	—	+ +	+ +	+ +	+ +
m-$NO_2C_6H_4$	p-$NO_2C_6H_4$	H	209—210	Prisms, dioxane	14.01, 14.17****	$C_{19}H_{14}O_9N_5P$	14.31 ****	=	=	=	=	+	+
p-$NO_2C_6H_4$	p-$NO_2C_6H_4$	H	178—179	Prisms, alcohol + dioxane	*****	$C_{19}H_{14}O_9N_5P$	*****	=	=	=	—	+	+
α-$C_{10}H_7$	C_6H_5	H	101—102	Needles, CCl_4	6.87, 7.03	$C_{23}H_{19}O_3N_2P$	6.93	—	+	+ +	+ +	+ +	+ +

* In the work [6] for four N-diaryloxyphosphinylarineamidines we consider the authors to have given incorrect melting points. The correct melting points are: N-diphenoxyphosphinyl-p-chlorobenzamidine 93-95°; N-diphenoxyphosphinyl-p-nitrobenzamidine 124-126°; N-phenyl-N-diphenoxyphosphinylbenzamidine 188-189°; N-phenyl-N'-diphenoxyphosphinyl-p-nitrobenzamidine 210-211°.

** Signs in Table 1.

*** Found %: Cl 7.62, 7.65. Calculated %: Cl 7.66.

**** Found %: P 6.51, 6.55. Calculated %: P 6.36.

***** Found %: P 6.45, 6.54. Calculated %: P 6.36.

$C_6H_5C[=NPO(OC_6H_5)_2]SC_6H_5 \longrightarrow C_6H_5SH + C_6H_5C[=NPO(OC_6H_5)_2]NHR$

RNH_2	$C_6H_5CH_2NH_2$	p-$CH_3C_6H_4NH_2$	$C_6H_5NH_2$	p-$ClC_6H_4NH_2$	p-$BrC_6H_4NH_2$	p-$NO_2C_6H_4NH_2$
$K_{base} \cdot 10^{10}$ [4]	$2.4 \cdot 10^5$	$2.0 \cdot 10$	4.6	1.5	1.0	$1.0 \cdot 10^{-2}$
Reaction time (hours)	18	22	25	25	25	33
Yield, %	91	75	59	48	16	4

$C_6H_5C[=NPO(OC_6H_5)_2]SR + C_6H_5NH_2 \longrightarrow RSH + C_6H_5C[=NPO(OC_6H_5)_2]NHC_6H_5$

RSH	p-$NO_2C_6H_4SH$	p-ClC_6H_4SH	C_6H_5SH
K_{acid} [5]	$7.76 \cdot 10^{-6}$	$1.10 \cdot 10^{-7}$	$1.74 \cdot 10^{-8}$
Reaction time (hours)	12	20	25
Yield, %	81	65	59

C. In 90% acetic acid. We heated a mixture of 0.0025 g mole of (I) and 5 ml of 90% acetic acid at 80° for two hours. After cooling, the diester precipitated and was filtered off and washed with water. By dilution of the mother liquor with water we isolated a further amount of diester. Total yield 80-90%.

In all cases the diesters of acylamidophosphoric acids were identified by mixed samples.

Reaction of (I) and aryl esters of diaryloxyphosphinyliminocarboxylic acids with ammonia (Tables 2 and 3). A suspension of 0.001 g mole of (I) or the aryl esters of diaryloxyphosphinyliminocarboxylic acids in 10-30 ml of alcohol was saturated with ammonia with stirring until the precipitate did not dissolve. In the case of the p-nitrophenyl esters the solution took on a yellow or red color. Reaction occurred with heating; after 10-15 minutes the reaction mixture was evaporated in a vacuum and the remaining solid substance (or oil which crystallized when treated with ether) was washed with ether to remove thiophenol or phenol, and was crystallized. The derivative of p-bromobenzoic acid was washed with a mixture of CCl_4 and ligroin (1 : 10). In the case of the p-nitrophenyl esters of diaryloxyphosphinyliminothiocarboxylic acids there remained after evaporation of the solvent a clear red oil which was washed with water to remove ammonium p-nitrothiophenolate.

Reaction of aryl esters of di-p-nitrodiphenoxyphosphinylimino-m-nitrobenzoic and thiobenzoic acids with ammonia (Tables 2 and 3). A suspension of 0.001 g mole of aryl ester of di-p-nitrodiphenoxyphosphinylimino-m-nitrobenzoic or thiobenzoic acid in 30 ml of alcohol was saturated with ammonia for six minutes. The mixture grew hot, the solution became yellow, the starting substance gradually dissolved, and a precipitate of difficultly soluble in alcohol N-di-p-nitrodiphenoxyphosphinyl-m-nitrobenzamidine appeared which was filtered off, washed with alcohol, and crystallized.

Reaction of (I) and aryl esters of N-diaryloxyphosphinyliminocarboxylic acids with amines (Tables 2 and 3). A mixture of 0.01 g mole of (I) or aryl ester of diaryloxyphosphinyliminocarboxylic acids, 0.04 g mole of amine, and 20-30 ml of alcohol was boiled under reflux (see Table 2). The solution became clear (in the case of p-nitrophenyl esters of diaryloxyphosphinyliminothiocarboxylic acid the solution became red). The reaction with the p-nitrophenyl ester of diaryloxyphosphinyliminothiocarboxylic acid must be carried out in the absence of oxygen, since the p-nitrothiophenol which is evolved is easily oxidized in an alkaline medium to a disulfide from which it is very difficult to purify the amidine. The reaction mixture was evaporated dry, to the solid residue we added ether, filtered the precipitate, washed with ether, and crystallized. In the case of p-nitrophenyl esters of diaryloxyphosphinyliminothiocarboxylic acids the solid residue was washed successively with water, dilute ammonia solution, water, and ether, and was dried and crystallized.

Preparation of N-diaryloxyphosphinylarineamidines from N-diaryloxyphosphinyliminoacyl chlorides. N-Di-p-nitrodiphenoxyphosphinyl-p-nitrobenzamidine (Table 4). A suspension of 0.01 g mole of N-di-p-nitrodiphenoxyphosphinylimino-p-nitrobenzoyl chloride in 50 ml of methylene chloride was saturated with dry ammonia (10 minutes). Reaction took place with heating. The precipitate of ammonium chloride was filtered off and washed with methylene chloride. The filtrate was evaporated in a vacuum and the solid residue was crystallized.

N-Di-p-nitrodiphenoxyphosphinyl-m-nitrobenzamidine (Table 4). The reaction was carried out in the same way as the preceeding. A considerable part

part of the amidine precipitated along with the ammonium chloride. Therefore the solvent was distilled off in a vacuum without separating the precipitate, the solid residue was washed with water and alcohol and dried and crystallized.

N-Diaryloxyphosphinylarineamidines of the type ArC[=NPO(OAr')$_2$]NHR (Table 4). A mixture of 0.01 g mole of N-diaryloxyphosphinyliminoacyl chloride, 0.02 g mole of amine, and 30-70 ml of dioxane was heated under reflux to disappearance of acid reaction to Congo in a sample mixed with water. The reaction mixture was poured into water, the precipitate was filtered off, washed with water, dried, and crystallized.

Reaction of (I) with nitric acid. To a solution of 0.002 g mole of (I) in 100 ml of CCl_4 with energetic stirring was added 0.005 g mole of nitric acid (d 1.5). After 36 hours the solution was evaporated in a vacuum at 20° (odor of thiophenol). In the residue was the corresponding diester of the acylamidophosphoric acid, which was washed with ether and recrystallized. Yield about 90%; identification with a mixed sample.

SUMMARY

1. In the reaction of N-diaryloxyphosphinyliminocarboxylic acid chlorides with sodium thiophenolates or with thiophenols in the presence of tertiary amines there are obtained aryl esters of N-diaryloxyphosphinyliminothiocarboxylic acids of the aromatic series which in their chemical properties resemble the aryl esters of N-diaryloxyphosphinyliminocarboxylic acids.

2. The sulfur in the esters of N-diaryloxyphosphinyliminothiocarboxylic acids does not have sulfide properties.

3. Aryl esters of N-diaryloxyphosphinyliminocarboxylic and thiocarboxylic acids in reaction with ammonia or amines exchange thioaryloxy or aryloxy groups (bound to the carbon atom) with the amino group, forming phenols or thiophenols and the corresponding N-diaryloxyphosphinylamidines.

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REACTION OF DIACYL CHLORIDES OF ALKYL PHOSPHINIC ACIDS WITH PHOSPHORUS PENTACHLORIDE

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In the previous communication [1] it was shown that when diacyl chlorides of aryl phosphinic acids react with PCl_5, crystalline complexes, $ArPCl_3^+ \cdot PCl_6^-$, are formed:

$$ArPOCl_2 + 2PCl_5 \longrightarrow ArPCl_3^+ \cdot PCl_6^- + POCl_3.$$

It was of interest to determine whether this reaction is specific only for diacyl chlorides of aromatic phosphinic acids or is general for diacyl chlorides of aryl and alkyl phosphinic acids. With this aim, we investigated the reaction of PCl_5 with diacyl chlorides of ethyl, propyl and butyl phosphinic acids. It was found that when phosphorus pentachloride reacts with diacyl chlorides of alkyl phosphinic acids under very mild conditions (in benzene, temperature 80°), not only conversion of the dichlorophosphinyl group to the $PCl_3^+ \cdot PCl_6^-$ group takes place, but also complete chlorination of the α-carbon atom, with formation of complexes of phosphorus pentachloride α,α-dichloroalkyl phosphorus tetrachlorides.

$$RCH_2POCl_2 + 4PCl_5 \longrightarrow 2HCl + 2PCl_3 + POCl_3 + RCCl_2PCl_3^+ \cdot PCl_6^-.$$

The position of the chlorine atoms in the alkyl groups shows that the action of sulfur dioxide on the complex $C_2H_3Cl_2PCl_3^+ \cdot PCl_6^-$ gives the diacyl chloride of dichloroethylphosphinic acid, identical to the diacyl chloride of α,α-dichloroethyl phosphinic acid obtained by Kinnear [2] by a method which leaves no doubt regarding its structure (see below).

$RCCl_2PCl_3^+ \cdot PCl_6^-$ complexes (Table 1) are colorless fine-crystalline substances with an odor of $POCl_3$, insoluble in ordinary organic solvents and reacting vigorously with alcohols and water. $RCCl_2PCl_3^+ \cdot PCl_6^-$ complexes hydrolyze at different rates, depending on the character of the radical. The complex $CH_3CCl_2PCl_3^+ \cdot PCl_6^-$ is hydrolyzed by water at 20° with release of about nine chlorine atoms. When this complex is boiled with water for 2 hours, about ten chlorine atoms are hydrolyzed; the final chlorine atom is not hydrolyzed by water, even with prolonged boiling. The complexes

$$C_2H_5CCl_2PCl_3^+ \cdot PCl_6^- \text{ and } n\text{-}C_3H_7CCl_2PCl_3^+ \cdot PCl_6^-$$

are more readily hydrolyzed than the complex with an α,α-dichloroethyl radical. When these complexes are boiled with water for 1 hour they are hydrolyzed with release of all the chlorine atoms.

When sulfur dioxide acts on the complexes

$$RCCl_2PCl_3^+ \cdot PCl_6^- (R = CH_3,\ C_2H_5,\ n\text{-}C_3H_7)$$

diacyl chlorides of α,α-dichloroalkyl phosphinic acids are formed.

$$RCCl_2PCl_3^+ \cdot PCl_6^- + 2SO_2 \longrightarrow POCl_3 + 2SOCl_2 + RCCl_2POCl.$$

TABLE 1. Complexes of Phosphorus Pentachloride with α,α-Dichloroalkyl Phosphorus Tetrachlorides of the Type $RCCl_2PCl_3^+ \cdot PCl_6^-$

R	Yield of the complex (%)	Yield of hydrogen chloride (equ.)*	Decomposition temp.	Found	Formula	Calculated
CH_3	70	1.7	100°	P%: 13.25, 12.85. Equ. after hydrolysis (20°, 24 hours): 11.65**; (100°, 2 hours): 13.65***	$C_2H_3Cl_{11}P_2$	P%: 12.95.
C_2H_5	19	1.7	115	Equ. after hydrolysis: 15.04, 14.96.	$C_3H_5Cl_{11}P_2$	Equ. after hydrolysis: 15.00.
$n\text{-}C_3H_7$	16	1.9	140	Cl%: 75.3. Equ. after hydrolysis: 15.40, 14.87.	$C_4H_7Cl_{11}P_2$	Cl%: 76.91. Equ. after hydrolysis: 15.00.

* Theoretical yield of hydrogen chloride 2.0 equ.

** Corresponds to ~2.35 atoms of unhydrolyzed chlorine.

*** Corresponds to ~1.35 atoms of unhydrolyzed chlorine.

TABLE 2. Monoalkyl Esters of Nomoacyl Chloride of α,α-Dichloroethyl Phosphinic Acid of the $CH_3CCl_2PO(OR)Cl$ type

R	Yield, %	B.p. (pressure in mm)	d_4^{20}	n_D^{20}	Found, %	Formula	Calculated, %
CH_3	14*	65—66° (3)	M.p. 40—41°	—	Cl 50.62. P 14.60, 13.82. CH_3O 13.3, 13.0.	$C_3H_6O_2Cl_3P$	Cl 50.00. P 14.65. CH_3O 14.65.
C_2H_5	61	82—83 (4)	1.3850	1.4698	P 13.50, 13.75. C_2H_5O 20.7. MR_D 45.4.	$C_4H_8O_2Cl_3P$	P 13.75. C_2H_5O 19.95. MR_D 44.9.
iso-C_3H_7	33**	68—70 (2.5)	1.3070	1.4600	P 13.09, 13.24. MR_D 50.2.	$C_5H_{10}O_2Cl_3P$	P 12.94. MR_D 49.5.
C_4H_9	25	104—105 (4)	1.3020	1.4690	Cl 41.84. P 12.17, 12.64 MR_D 54.2.	$C_6H_{12}O_2Cl_3P$	Cl 42.10. P 12.23. MR_D 54.1.

* Synthesized by the action of diacyl chloride on methanol in the absence of tertiary bases.

** Obtained in the presence of triethylamine.

The diacyl chloride of α,α-dichloroethyl phosphinic acid $CH_3CCl_2POCl_2$ (I) was first obtained by Kinnear [2], but with the exception of its melting point he did not describe the properties. (I) is a colorless crystalline substance which distils under vacuum, has a marked lachrimatory effect, is very difficultly soluble in cold water and readily soluble in organic solvents. In its physical and chemical properties (I) resembles the diacyl chloride or trichloromethyl phosphinic acid [3]. Hydrolysis of (I) by water at room temperature takes place with release of only one chlorine atom; when it is boiled with water for 1 hour a second chlorine atom is hydrolyzed. With prolonged boiling (~10 hours), three chlorine atoms are released. When (I) is acted on by alcohols in the presence of pyridine, only one

acyl-chloride chlorine atom is substituted by alkoxyl, with formation of monoalkyl esters of the monoacyl chloride of α,α-dichloroethyl phosphinic acid (II).

$$CH_3CCl_2POCl_2 \xrightarrow[R = CH_3,\ C_2H_5,\ iso\text{-}C_3H_7,\ n\text{-}C_4H_9]{+ROH + C_5H_5N} CH_3CCl_2PO(OR)Cl$$

Substance (II) is colorless liquid (with the exception of the crystalline methyl ester (m.p. 40-41°) with a fruity odor (Table 2), with insecticidal properties. After it has been boiled with water for 30 minutes their hydrolysis products are estimated volumetrically and require two equivalents; therefore during this process the acyl-chloride chlorine atom is released and the methoxyl group is probably not split off. (II) distils under vacuum (2-3 mm), but more than half the substance polymerizes with the formation of vitreous or power-like yellowish polymers, soluble in water.

The diacyl chlorides of α,α-dichloropropyl phosphinic and α,α-dichlorobutyl phosphinic acids are slightly greenish oily liquids with an unpleasant acrid odor, hydrolyzing rapidly in air. In contrast to the diacyl chloride of α,α-dichloroethyl phosphinic acid, the diacyl chlorides of α,α-dichloropropyl- and α,α-dichlorobutyl phosphinic acids release all four chlorine atoms when boiled with water for 1.5 hours.

As a result of complete hydrolysis of the diacyl chloride of α,α-dichlorobutyl phosphinic acid or the complex $N\text{-}C_3H_7CCl_2PCl_3^+ \cdot PCl_6^-$ a crystalline substance with an m.p. of 173-174° is obtained, which in properties and composition is an α-ketobutyl phosphinic acid.

$$n\text{-}C_3H_7CCl_2PCl_3 \cdot PCl_6 + 7H_2O \longrightarrow 9HCl + H_3PO_4 + n\text{-}C_3H_7COP(OH)_2$$

Thus, in contrast to α-ketobenzyl phosphinic acid—which, according to M. I. Kabachnik and P. A. Rossiiskaya, decomposes into benzoic and phosphinic acids in aqueous acid solutions [4]—α-ketobutyl-phosphinic acid is stable in the latter.

We did not succeed in obtaining the corresponding ketophosphinic acid in the individual state by hydrolysis of $CH_3CH_2CCl_2PCl_3^+ \cdot PCl_6^-$ and the diacyl chloride of α,α-dichloropropyl phosphinic acid. As a result of hydrolysis of these compounds, an oil, which does not crystallize, is obtained. This does not contain chlorine and it has not been possible as yet to isolate individual substances from it.

EXPERIMENTAL

Preparation of complexes of the type $RCCl_2PCl_3^+ \cdot PCl_6^-$ (R = CH_3, C_2H_5, N-C_3H_7) (Table 1). A solution of 0.15 g-mole of the diacyl chloride of alkyl phosphinic acid [5] in 20 ml of benzene was added in 5 minutes with mechanical stirring to a boiling solution of 0.75 g-mole of PCl_5 in 300 ml of dry benzene. A colorless fine-crystalline precipitate began to form in the transparent solution after 10 minutes, and hydrogen chloride was liberated. Boiling and stirring of the reaction mixture was continued for 6 hours. The hydrogen chloride was removed and determined by the usual methods. The crystalline product was rapidly filtered from the hot reaction mixture under dry air. The complexes were fine-crystalline substances with an odor of $POCl_3$, hydrolyzing rapidly in air, insoluble in ordinary organic solvents, and reacting rapidly with alcohols and water. When heated, they decomposed without melting.

Preparation of the diacyl chloride of α,α-dichloroethyl phosphinic acid (I). We placed 0.2 g-mole of the complex $CH_3CCl_2PCl_3^+ \cdot PCl_6^-$ in a round-bottomed flask and a slow current of sulfur dioxide (dried over P_2O_5) was passed for 4 hours, which cooling by ice water. The crystalline complex was gradually converted to a green liquid. The $POCl_3$ and $SOCl_2$ were driven off under vacuum. The residue was the diacyl chloride of α,α-dichloroethyl phosphinic acid (I) in the form of colorless crystals; (I) has an acrid odor and is a lacrimator, soluble in ordinary organic solvents, difficultly soluble in cold water. It sublimes under vacuum (30 mm, 125-130°). The yield of crude (I) was 74%, while that of the sublimed was 62%; the m.p. was 147-148° (according to [2] it is 147-150°).

Found %: Cl 66.49, 66.03; P 14.06, 14.16. M 239, 194. $C_2H_3OPCl_4$. Calculated %: Cl 65.74; P 14.35. M 216.

After hydrolysis at 20° (I) titrates to 2.10 equ., and after boiling with water for 10 hours, to 5.00 equ. Therefore at 20° about three chlorine atoms remain in the molecule, while one chlorine atom is left after boiling.

Monoalkyl esters of the monoacyl chloride of α,α-dichloroethyl phosphinic acid (II). A mixture of 0.14 g-mole of the corresponding alcohol and 0.14 g-mole of pyridine in 20 ml of benzene was added for 40 minutes (with cooling by ice water) to a solution of 0.07 g-mole of the diacyl chloride of α,α-dichloroethyl phosphinic acid in 50 ml of dry benzene. A precipitate of the hydrogen chloride salt of pyridine came out immediately. After the addition of the solution of alcohol and pyridine the reaction mixture was stirred for a further hour with cooling by ice water and then for 1 hour at 20°. The yield was theoretical. The pyridine hydrochloride was filtered at the pump, and washed with benzene. The filtrate was washed with water (5 x 10 ml), dried with calcium chloride and evaporated under vacuum. The residue was distilled under vacuum. Triethylamine may be used as the tertiary amine instead of pyridine. The methyl ester was obtained by the action of the diacyl chloride of α,α-dichloroethyl phosphinic acid (0.05 g-mole) on methanol (20 ml) at 20°. After 24 hours the solvent was driven off under vacuum and the residue was distilled at 3 mm. We did not succeed in obtaining the isopropyl ester in this way; the reaction took place only after addition of the tertiary amine.

The diacyl chlorides of α,α-dichloropropyl- and α,α-dichlorobutylphosphinic acids were obtained in the same way as (I). After $POCl_3$ and $SOCl_2$ had been driven off, the liquid diacyl chlorides were distilled under vacuum. They were slightly greenish oily liquids with an unpleasant acrid odor, fuming in air and soluble in ordinary organic solvents. They react vigorously with water.

Diacyl chloride of α,α-dichloropropylphosphinic acid: Yield 80%, b.p. 115-116° (4 mm), d_4^{20} 1.6190, n_D^{20} 1.5400.

Found: equ. after hydrolysis 6.02, 5.94, MR_D 44.6. $C_3H_5OCl_4P$. Calculated: equ. after hydrolysis 6.00. MR_D 43.8.

Diacyl chloride of α,α-dichlorobutylphosphinic acid; yield 45%, b.p. 116-118° (2.5 mm), d_4^{20} 1.5740, n_D^{20} 1.5140.

Found: equ. after hydrolysis 5.92, 6.12. MR_D 48.2. $C_4H_7OCl_4P$. Calculated: equ. after hydrolysis 6.00. MR_D 48.5.

α-Ketobutylphosphinic acid. We mixed 0.005 g-mole of the complex $N\text{-}C_3H_7CCl_2PCl_3^+ \cdot PCl_6^-$ with 5 ml of water at room temperature. The reaction was exothermic. The water was evaporated under vacuum at 60-70°. The residue consisted of 1.08 g of a chlorine-free crystalline mass, impregnated with liquid, which corresponded to the over-all theoretical yield of α-ketobutylphosphinic and phosphoric acids. The product was recrystallized twice from glacial acetic acid. α-Ketobutylphosphinic acid is a colorless crystalline substance (needles); m.p. 173-174°, readily soluble in water and ordinary organic solvents.

Found α: P 20.43. Equ. 2.03. $C_4H_9O_4P$. Calculated α: P 20.4. Equ. 2.00.

SUMMARY

1. As a result of the action of phosphorus pentachloride on diacyl chlorides of alkyl phosphinic acid, simultaneous conversion of the dichlorophosphinyl group to $PCl_3^+ \cdot PCl_6^-$ and complete chlorination of the α-carbon atom take place, and complexes of phosphorus pentachloride with α,α-dichloroalkylphosphorus tetrachlorides of the type

$$RCCl_2PCl_3^+ \cdot PCl_6^-.$$

2. When the complex $CH_3CCl_2PCl_3^+ \cdot PCl_6^-$ is boiled with water, one atom of chlorine is not released, whereas in the case of complexes with R = C_2H_5 or $N\text{-}C_3H_7$ the chlorine is completely removed.

3. As a result of hydrolysis with water, the complex $N\text{-}C_3H_7CCl_2PCl_3^+ \cdot PCl_6^-$ and the diacyl chloride of α,α-dichlorobutylphosphinic acid give a crystalline α-ketobutylphosphinic acid.

4. When acted on by sulfur dioxide the complexes $RCCl_2PCl_3^+ \cdot PCl_6^-$ are converted to the diacyl chloride of α,α-dichloroalkylphosphinic acids.

5. When alcohols act on the diacyl chloride of α,α-dichloroethylphosphinic acid, only one acyl-chloride chlorine atom takes part in the reaction and monoalkyl esters of the monoacyl chloride of α,α-dichloroethylphosphinic acid, with insecticidal properties, are formed.

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N-DICHLOROPHOSPHINYLCARBAMIC ACID

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Carbamic acid and N-substituted carbamic acids are only stable in the form of salts, esters and other derivatives, and in the free state they decompose with the formation of carbon dioxide and the corresponding amino compounds [1]. Therefore it might be expected that N-dichlorophosphinylcarbamic acid, which must be formed when water acts on the diacyl chloride of isocyanophosphoric acid, would readily split off carbon dioxide, being converted to the diacyl chloride of phosphamic acid.

$$Cl_2PONCO + H_2O \longrightarrow [Cl_2PONHCOOH] \longrightarrow Cl_2PONH_2 + CO_2$$

Experiments showed that as a result of the action of excess water the diacyl chloride of isocyanophosphoric acid does in fact readily split off carbon dioxide, but that hydrolysis of the acyl chloride part of the molecule takes place simultaneously

$$Cl_2PONCO + 4H_2O \longrightarrow CO_2 + 2HCl + NH_4H_2PO_4$$

In the case of the reaction with 1 g-mole of water in different solutions and under very varied conditions it was impossible to limit the reaction to the addition of water to the isocyanate group and obtain clear and reproducible results. It was possible to add water to the isocyanate group only, without hydrolysis of the chlorine atoms combined with phosphorus, by employing R. Graf's method [2], which he proposed for the hydrolysis of the acyl chloride of isocyanosulfuric acid, i.e., by using concentrated hydrochloric acid as the source of water. In this way the very thermally stable N-dichlorophosphinylcarbamic acid (I) is obtained from the diacyl chloride of isocyanophosphoric acid.

$$Cl_2PONCO \xrightarrow{+H_2O} \underset{(I)}{Cl_2PONHCOOH}$$

In contrast to all other known N-substituted carbamic acids, this acid remains unchanged at 4-6°, and at room temperature only decomposes slowly with liberation of hydrogen chloride (see below). (I) is a colorless crystalline substance (fine prisms), insoluble in ordinary organic solvents, readily hydrolyzed by water or atmospheric moisture, with liberation of hydrogen chloride and carbon dioxide. When heated, (I) melts at 73-74° (with decomp.). The structure of (I) is proven by analytical data and the following reactions.

1. Complete hydrolysis gives carbon dioxide, phosphoric acid, ammonia and hydrogen chloride

$$Cl_2PONHCOOH \xrightarrow{+3H_2O} 2HCl + NH_3 + CO_2 + H_3PO_4$$

2. When acted on by phosphorus pentachloride, an almost quantitative yield of the diacyl chloride of isocyanophosphoric acid, phosphorus oxychloride and hydrogen chloride is obtained

$$Cl_2PONHCOOH \xrightarrow{+PCl_5} \underset{(85\%)}{2HCl} + \underset{(90\%)}{POCl_3} + \underset{(50\%)}{Cl_2PONCO}$$

3. The action of alcohols gives a nearly quantitative yield of trialkyl phosphates (in this case the NHCOOH group behaves like a pseudohalogen)

$$Cl_2PONHCOOH \xrightarrow{+3ROH} HCl + \underset{(95\%)}{NH_4Cl} + CO_2 + \underset{(90\%)}{(RO)_3PO}$$

4. As a result of the action of aniline on (I) the aniline salt of N-dianilidophosphinylcarbamic acid is obtained. We did not succeed in obtaining this in the pure state but its structure is not doubtful, because caustic soda converts the aniline salt to the sodium salt of dianilidophosphate, sodium carbonate, aniline and ammonia being liberated:

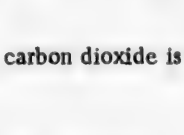
$$Cl_2PONHCOOH \xrightarrow{+5C_6H_5NH_2} (C_6H_5NH)_2PONHCOONH_3C_6H_5 \xrightarrow{+3NaOH}$$
$$\rightarrow (C_6H_5NH)_2POONa + NH_3 + Na_2CO_3 + C_6H_5NH_2 + H_2O$$

Dianilidophosphamate (4 %), trianilidophosphate (6%) and symm.-diphenyl urea (9%) are produced as by-products of this reaction. Dianilidophosphamate is not described in the literature and it was therefore synthesized from dianilidochlorophosphate and ammonia (see EXPERIMENTAL).

5. When heated at atmospheric pressure, (I) splits off hydrogen chloride, about 30% of the diacyl chloride of isocyanophosphoric acid being formed; solid products containing chlorine are also obtained, but it has hitherto been impossible to isolate individual substances from these. When it is heated under vacuum to 160°, hydrogen chloride is split off and the diacyl chloride of isocyanophosphoric acid (80%) and polymeric N-carboxylmetaphosphimic acid (anhydro-N-carboxyphosphamic acid) (II) are formed.

$$2Cl_2PONHCOOH \xrightarrow{160^\circ} 2HCl + Cl_2PONCO + \frac{1}{x}\underset{(II)}{[HOPO(=NCOOH)]_x}$$

The acid (II) is a colorless, amorphous substance which does not melt when heated to 400°; it is readily hydrolyzed by moist air and is insoluble in any of the ordinary organic solvents. N-carboxylmetaphosphimic acid (II) probably has the following type of structure.



When (II) is heated under vacuum to 500°, carbon dioxide is split off and the acid is converted to metaphosphimic acid.

$$[HOPO(=NCOOH)]_x \xrightarrow{500^\circ} [-NH-PO(OH)-]_x \rightleftarrows [-N=P(OH)_2-]_x$$

The physical and chemical properties of the metaphosphimic acid obtained in this way are identical with those of the metaphosphimic acid described in the literature [3].

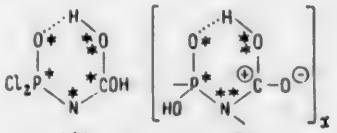
When metaphosphimic acid is heated to 1000-1100° in a platinum crucible, water is split off and it is converted to the polymeric oxynitride of phosphorus, identical to that described in the literature [4].

$$[-NH-PO(OH)-]_x \rightarrow (PON)_x$$

Thus, when N-dichlorophosphinylcarbamic acid is heated the following processes take place in succession:

$$2Cl_2PONHCOOH \xrightarrow{160^\circ} Cl_2PONCO + \frac{1}{x}[HOPO(=NCOOH)]_x \xrightarrow{500^\circ}$$
$$\rightarrow \frac{1}{x}(HOPONH)_x \xrightarrow{1000^\circ} \frac{1}{x}(PON)_x$$

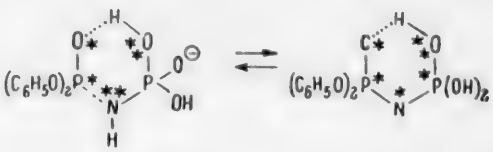
The extreme thermal stability of N-dichlorophosphinylcarbamic acid is probably due to the particular strength of the hydrogen bond in the ring, caused by the general structural characteristics of the molecule. The ring system of N-dichlorophosphinylcarbamic acid may have an aromatic character to some extent, because the six atoms forming the ring have six π-electrons (indicated by an asterisk) which may form an aromatic system, provided that the hydrogen atom in this molecule can be a "conductor" for this system (A).



(A) (B)

The still greater thermal stability of N-carboxymetaphosphimic acid may be explained in a similar way, but in this case the "aromatic" ring must have a positive charge, while the oxygen atom is negative, similar to that found in sidnones [5] and other similar rings (B).

The unusual resistance to hydrolysis, and the low solubility in water of the p,p-diphenyl ester of imidodiphosphoric acid [6] is also probably due to its "aromatic" structure with a hydrogen bond forming part of the ring.



The aromatic system of all these compounds is distinguished from the ordinary aromatic system by the fact that a hydrogen bond and a hydrogen atom form part of the ring, and that one of the π-electrons of the aromatic sextet belongs to the d-level (electron of the phosphorus atom), not the p-level (see [7]). Further investigations will show just how correct are these novel assumptions.

EXPERIMENTAL

N-Dichlorophosphinylcarbamic acid. We added 12.4 ml of 36% hydrochloric acid (~15 minutes) with vigorous stirring and cooling to -20° to a solution of 0.5 g-mole of the diacyl chloride of isocyanatophosphoric acid in 500 ml of CCl_4. A colorless crystalline precipitate soon began to form. After all the hydrochloric acid had been added the temperature of the reaction mixture was allowed to rise with constant stirring to 20° for 1 hour. To obtain good yields it was necessary to continue stirring at 20° until liberation of hydrogen chloride had completely ceased (~1.5 hours). N-Dichlorophosphinylcarbamic acid was rapidly filtered at the pump in an atmosphere of dry air, washed with CCl_4 and dried under vacuum at room temperature. The yield was 96%; colorless fine prisms, m.p. 73-74° (decomp.). The acid is insoluble in ordinary organic solvents.

Found %: N 7.73, 7.76; P 17.82, 17.90; Cl 39.90, 40.42. $CH_2O_3NCl_2P$. Calculated %: N 7.86; P 17.41; Cl 39.89.

Reaction of N-Dichlorophosphinylcarbamic acid with phosphorus pentachloride. We mixed 0.2 g-mole of N-dichlorophosphinylcarbamic acid and 0.2 g-mole of PCl_5 in a round-bottomed flask. Vigorous liberation of hydrogen chloride took place immediately and the reaction mixture became liquid. After 15 minutes the rate of gas liberation decreased appreciably. The mixture was heated slowly to 80° and kept at this temperature until liberation of hydrogen chloride had ceased (30 minutes). Distillation gave phosphorus oxychloride (90%) and the diacyl chloride of isocyanatophosphoric acid (90%). The yield of hydrogen chloride was 85%.

Reaction of N-dichlorophosphinylcarbamic acid with alcohols. We added 0.03 g-mole of N-dichlorophosphinylcarbamic acid to 30 ml of anhydrous methyl, ethyl or N-propyl alcohol. As the acid dissolved, the solution became hotter and a precipitate of ammonium chloride appeared. After 6-8 hours the precipitate was filtered and washed with the corresponding alcohol (2 x 5 ml). The filtrate was evaporated under vacuum at 50° and the residue was distilled under vacuum. In this way we obtained: trimethyl phosphate, b.p. 73-74° (10 mm) [8], n_D^{20} 1.3968 [9], yield 81%; triethyl phosphate, b.p. 90-91° (10 mm) [8], n_D^{20} 1.4055 [9], yield 86%; tri-N-propyl phosphate, b.p. 121-122° (10 mm) [8]), n_D^{20} 1.4167 [9], yield 84%.

Reaction of N-dichlorophosphinylcarbamic acid with aniline. We added 0.05 g-mole of N-dichlorophosphinylcarbamic acid with vigorous stirring to 0.25 g-mole of aniline, cooled with ice, and the mixture was heated for 10-15 minutes at 140-150° until a homogeneous solution was formed. After it had been cooled, the solution was added with stirring to 250 ml of 10% hydrochloric acid. The aniline hydrochloride dissolved and the reaction product was precipitated as an oil, which gradually crystallized. After it had stood for a day the solid substance was filtered at the pump, triturated in a mortar with 10% HCl (3 x 15 ml), filtered and dried. The yield of the crude aniline salt of N-anilidophosphinylcarbamic acid was 20 g, the m.p. was 160-190°. We did not succeed in purifying the substance. The salt was mixed with 100 ml of 1 N caustic soda and the aniline formed was steam distilled. The aniline was extracted from the distillate with ether (2 x 50 ml). The aniline yield was 72%. After the alkali-insoluble precipitate had been cooled it was filtered at the pump, washed with 1 N caustic soda (2 x 5 ml) and dried. After several recrystallizations from alcohol, trianilido phosphate (6%), symm.-diphenyl urea (9%) and dianilido phosphamate (4%) were obtained; these were identified by means of a mixed melting point. After the precipitate had been separated the alkaline filtrate was evaporated under vacuum to ~15 ml. 150ml of alcohol was added to the cooled solution; the sodium carbonate precipitated by this was filtered, washed with alcohol (2 x 5 ml) and dried. The yield was 72%. After the soda had been separated the filtrate was evaporated to dryness. The residue was the sodium salt of dianilidophosphoric acid (72%). When an aqueous solution of the salt was acidified, free dianilidophosphoric acid was precipitated (65%); identification was by means of a mixed sample.

Dianilidophosphamate. A mixture of 0.02 g-mole of dianilidochlorophosphate and 50 ml of a concentrated aqueous solution of ammonia was stirred for 15 minutes. The precipitate was filtered, washed with water (5 x 20 ml) and dried. The yield was 52%. Dianilidophosphamate consists of lustrous colorless plates with an m.p. of 210-212°. It dissolves when heated in water, alcohol, acetone, dioxan; it is difficultly soluble in benzene and chloroform, and insoluble in ether, CCl_4 and petroleum ether.

Found %: N 16.94, 16.80; P 12.48, 12.39. $C_{12}H_{14}ON_3P$. Calculated %: N 17.00; P 12.55.

Thermal decomposition of N-dichlorophosphinylcarbamic acid. A. N-Carboxylmetaphosphimic acid. We placed 0.2 g-mole of N-dichlorophosphinylcarbamic acid in a flask connected in turn to a U-tube filled with P_2O_5 and glass wool, a trap, cooled to -80°, a protective flask and a flask filled with a caustic soda solution to absorb HCl. The system was evacuated and the flask with the acid was heated slowly to 100° for 20 hours and then to 160° for 10 hours. The liberated hydrogen chloride was titrated at intervals of 2 hours. The experiment was continued until no more hydrogen chloride was liberated. The weight of the U-tube did not vary, indicating that water was not formed during the reaction. 0.07 g-mole (70%) of the diacyl chloride of isocyanatophosphate acid was collected in the trap. The hydrogen chloride yield was 130%; the value was too high because the diacyl chloride of isocyanatophosphoric acid passed through together with the hydrogen chloride. Assuming that not more than 100% of hydrogen chloride could be produced, it can be calculated that the hydrogen chloride entrained about 10% of the diacyl chloride of isocyanatophosphoric acid, and the total yield of the latter was therefore about 80%. The yield of N-carboxylmetaphosphimic acid was almost quantitative. The acid was a colorless amorphous substance which did not melt when heated to 400°; it was insoluble in ordinary organic solvents. It was decomposed by water or atmospheric moisture.

Found %: N 11.64, 11.72; C 9.18, 9.60; H 1.09, 1.23; P 25.58, 25.76. CH_2O_4NP. Calculated %: N 11.38; C 9.75; H 1.63; P 25.20.

B. Polymetaphosphimic acid. We placed 0.1 g-mole of N-carboxylmetaphosphimic acid in a flask, connected to the outlet tube, immersed in a solution of barium hydroxide; it was then heated on a gas burner to 500°. A precipitate of barium carbonate was formed. Towards the end, heating was continued under vacuum to constant weight. The yield of polymetaphosphimic acid was quantitative. The acid was a fine-crystalline, incombustible, non-fusible substance, difficultly soluble in cold water and alkalis and insoluble in acids and ordinary organic solvents. It gives an acid reaction with congo and is hygroscopic. When aqueous solutions of Fe^{+++}, Ag, Mg, Zn, Al, Cu^{+++} or Ba salts are added to an aqueous solution of polymetaphosphimic acid, water-insoluble metallic salts of polymetaphosphimic acid are formed.

Found %: N (by Kjeldahl) 17.64, 17.58; P 39.46, 39.52. H_2O_2NP. Calculated %: N 17.72; P 39.24.

C. Phosphorus oxynitride. We heated 0.02 g-mole of polymetaphosphimic acid in a platinum crucible at 1000-1100°. After 1 hour the solid substance obtained (1.41 g) was transferred to a mortar, triturated with cold water to remove P_2O_5, filtered at the pump and dried. The yield of phosphorus oxynitride was 85%.

Found %: N (by Kjeldahl) 22.85, 22.71; P 48.68, 49.52. PON. Calculated %: N 22.95; P 50.82.

SUMMARY

1. When the diacyl chloride of isocyanophosphoric acid reacts with 1 g-mole of water contained in concentrated hydrochloric acid, relatively thermally stable N-dichlorophosphinylcarbamic acid is obtained.

2. Phosphorus pentachloride converts N-dichlorophosphinylcarbamic acid almost quantitatively to the diacyl chloride of isocyanophosphoric acid.

3. The reaction of N-dichlorophosphinylcarbamic acid with alcohols gives trialkyl phosphates. During this reaction the NHCOOH group behaves likes a pseudohalogen.

4. When acted on by alkali, the aniline salt of N-dianilidophosphinylcarbamic acid, formed from N-dichlorophosphinylcarbamic acid and aniline, hydrolyzes with formation of the sodium salt of anilidophosphoric acid, aniline, sodium carbonate and ammonia.

5. When N-dichlorophosphinylcarbamic acid is heated to 160°, hydrogen chloride is split off and the diacyl chloride of isocyanatophosphoric acid and polymeric N-carboxylmetaphosphimic acid are formed. The latter splits off carbon dioxide only at 500° and is converted to polymetaphosphimic acid, which when heated to 1000-1100° loses water, with formation of phosphorus oxynitride.

6. The thermal stability of N-dichlorophosphinylcarbamic acid and N-carboxylmetaphosphimic acid is probably explained by the fact that they have an aromatic structure with a hydrogen bond forming part of the ring.

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SECONDARY ACETYLENE ALCOHOLS OF THE Δ^3-CYCLOHEXENE SERIES AND SOME OF THEIR CONVERSIONS

G. P. Kugatova, V. V. Mozolis and Z. B. Alaune

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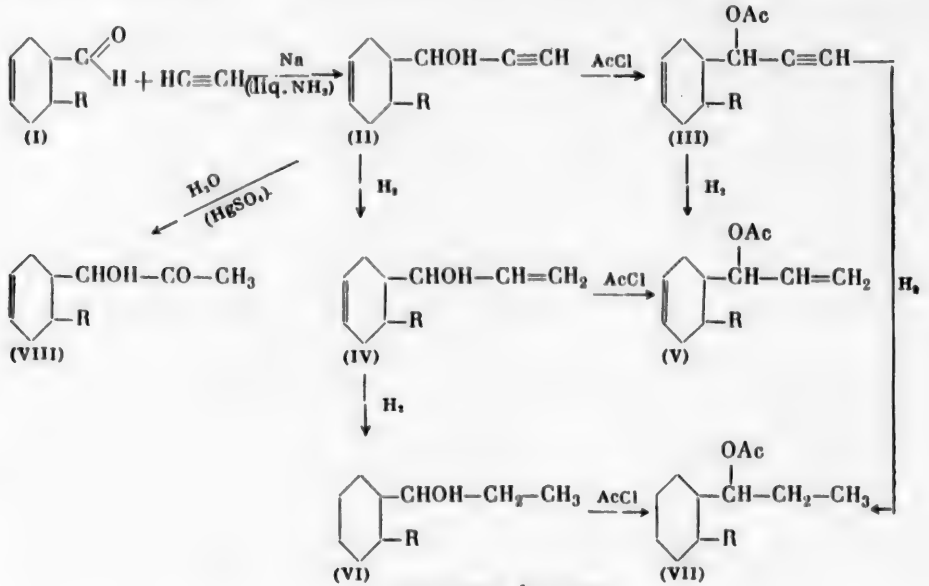
Information on secondary acetylene alcohols of the Δ^3-cyclohexene series is confined to patent literature [1], dealing with their synthesis and use as corrosion inhibitors and insecticides. The comparative ease with which this series of acetylene alcohols is obtained, on the basis of Δ^3-cyclohexanols, and the possibility of using them as intermediates in the synthesis of polyene systems of similar structure to certain natural substances justified an investigation of the chemistry of this class of compounds.

Secondary acetylene alcohols were obtained with good yields by condensation of sodium acetylide and Δ^3-cyclohexanol (I) in liquid ammonia. In this process, together with the corresponding acetylene alcohols (II) a nitrogen-containing substance is always formed; the amount of the latter can be reduced considerably by increasing the volume of liquid ammonia and using dimethoxymethane as solvent for the aldehyde.

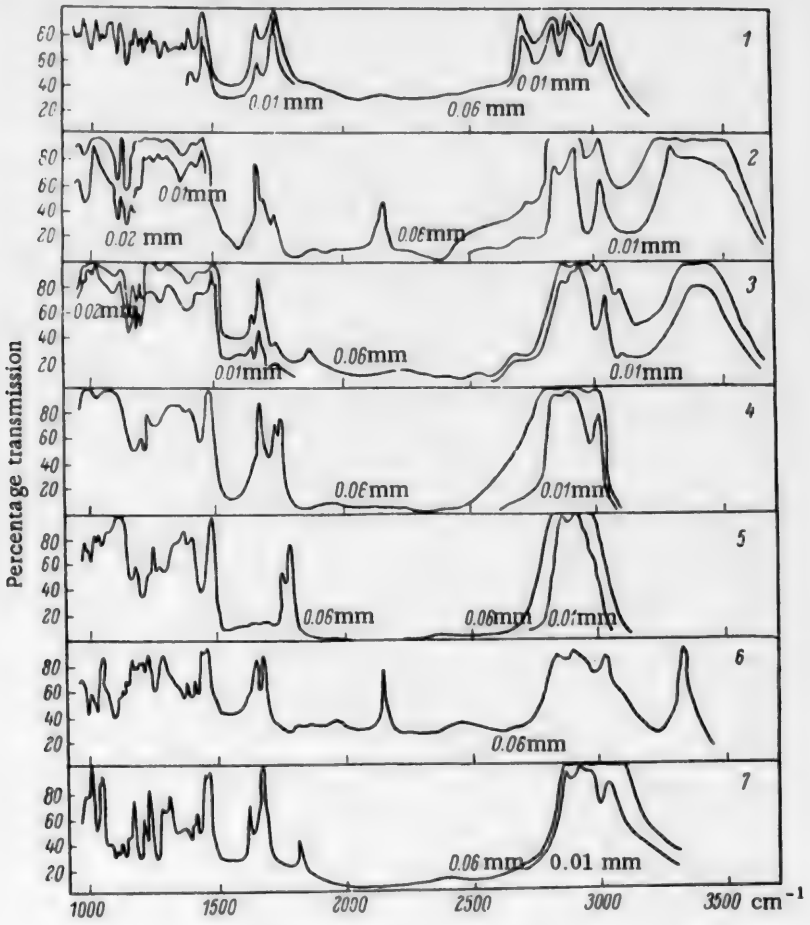


a) R = CH_3, b) R = H.

The structure of the synthesized substances was confirmed by an investigation of their infrared absorption spectra in the 900-4000 cm^{-1}* region (Fig. 1), and by studying their properties and conversions. The large amount of literature data available [2] was used for interpreting the characteristic absorption bands of the C = C and C ≡ C bonds. The 1654 cm^{-1} band was attributed to the C = C valence vibration in the ring, this absorption band was observed both in the case of the initial aldehyde (Ib) and for all the investigated substances containing a Δ^3-cyclohexene ring, i.e., (IIb), (IVb), (XIb), (XIIIb) and (XIVb). The 2117 cm^{-1} band, observed in the case of acetylene alcohol (IIb), is characteristic of unconjugated monosubstituted acetylene compounds, which generally show absorp-

* The spectra were determined in an IKS-12 single-beam spectrometer with a prism of liquid sodium chloride, the layer thickness being 0.01-0.06 mm.

tion in the 2100-2140 cm^{-1} region. Finally, the absorption band with a frequency of 3298 cm^{-1} confirms the presence in the alcohol (IIb) of acetylene hydrogen, the valence vibrations for which generally lie in the 3290-3390 cm^{-1} range.



Infrared absorption spectra

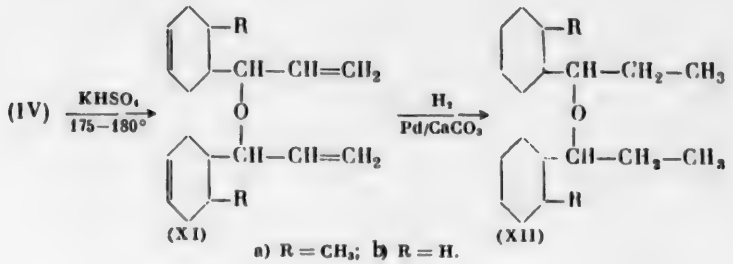
Infrared absorption spectra: 1) Δ^3-Tetrahydrobenzaldehyde (Ib); 2) 3-(cyclohexene-Δ^3-il)-propine-1-ol-3 (IIb); 3) 3-(cyclohexene-Δ^3-il)-propene-1-ol-3 (IVb); 4) di-3-(cyclohexene-Δ^3-il)-propene-1-il ester (XIb); 5) 1,1'-dicyclohexylpropyl ester (XIIb); 6) 3-(cyclohexene-Δ^3-ylen)-propin-1 (XIIIb); 7) 3-(cyclohexene-Δ^3-ylen)-propylene-1 (XIVb).

Acetylene alcohols (II) are readily hydrogenated in the presence of a palladium catalyst into the corresponding saturated alcohols (VI); but with hydrogenation by 1 mole of hydrogen the corresponding diene alcohols (IV) are formed. The distinctly selective hydrogenation of the initial acetylene alcohol (IIb) and the character of the infrared spectra of the diene alcohol obtained (IVb) (absence of absorption bands of C ≡ C and ≡C−H valence vibrations and the appearance of a new band at 1625 cm^{-1}, characteristic of the C = C bond) indicate the presence of a double bond in the side chain in the case of the latter.

According to Kucherov, the hydration of secondary acetylene alcohols (II) takes place normally, giving a fairly high yield of the corresponding ketols (VIII).

In contrast to the dehydration of tertiary acetylene alcohols, the dehydration of secondary acetylene alcohols has been little investigated. In the literature there are indications that aliphatic secondary acetylene alcohols are dehydrated at high temperature to vinylacetylene hydrocarbons [4]. When certain authors [1] made attempts to carry out the dehydration of acetylene alcohols obtained on the basis of Δ^3-cyclohexanol by thermal treatment in the liquid or vapor phase, products of intense decomposition of the initial compounds were obtained.

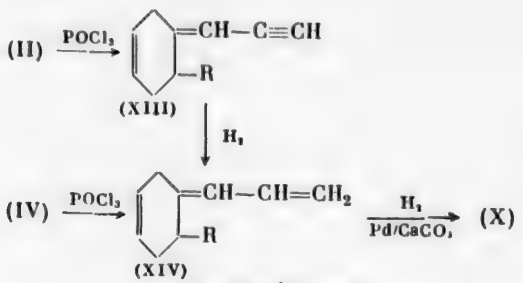
When the dehydration reaction of acetylene alcohols (II) and the products of their complete or partial hydrogenation (IV) and (VI) were investigated it was noted that dehydration with potassium bisulfate takes place normally only with saturated alcohols (VI).



a) $R = CH_3$; b) $R = H$.

When the latter were heated at 180-190°, unsaturated hydrocarbons (IX) were obtained, hydrogenation of which gave saturated hydrocarbons. At the same time, dehydration of diene alcohols (IV) with potassium bisulfate at 175-180° gave unsaturated ethers (XI), which during hydrogenation with $Pd/CaCO_3$ absorbed 4 moles of hydrogen, being converted to the saturated ethers (XII). In the region of absorption of the ether bond the infrared spectra of the ethers obtained and fairly strong bands at 1055 and 1098 cm^{-1}, in the case of (XIb), and at 1086 cm^{-1} for (XIIb).

Under these conditions, acetylene alcohols (II) are not dehydrated. Attempts to dehydrate them with phosphorus pentoxide and with ammonium sulfate in the vapor phase were not successful. But acetylene (II) and diene alcohols (IV) can be dehydrated with phosphorus pentoxide in pyridine, although the yield is relatively low as a result of the great difficulty in removing chlorine-containing by-products.



a) $R = CH_3$; b) $R = H$

The dehydration of acetylene alcohols takes place for the most part in the same direction and is not accompanied by isomerization of the multiple bonds. The principal dehydration products are the compounds (XIII), the structure of which was proven by an investigation of their infrared spectra. It is known that as a result of conjugation of a double bond with a tertiary one the frequency of the latter is reduced by approximately 10-15 cm^{-1} and its strength increases [3]. In the dehydration product (XIIIb) the absorption band of the valence vibration of the triple bond was reduced by approximately 12 cm^{-1} and was strengthened considerably compared with the triple bond in acetylene alcohol (IIb), which makes it possible to assess the structure of the side chain in the compound obtained. For compound (XIIIb), in the absorption region of double bonds there are two bands: one at 1633 cm^{-1}, the other at 1652 cm^{-1}. Thus the spectral data obtained indicate that the side chain of the dehydration product (XIIIb) has conjugated multiple bonds.

The dehydration of diene alcohols (IV) takes place similarly to the dehydration of acetylene alcohols (II), being unaccompanied by isomerization. As a result of this reaction, compound (XIV) is formed, which was proven

No. of substance	Compound obtained	B.p. (pressure in mm)	n_D^{20}	d_4^{20}	MR_D found	MR_D calc.	Found, % C	Found, % H	Empirical formula	Calc., % C	Calc., % H
IIa	3-(6'-Methylcyclohexenyl-3)-propine-1-ol-3	77—78° (1)	1.4988	0.9827	45.27	45.24	80.24, 80.20	9.50, 9.29	$C_{10}H_{14}O$	80.00	9.33
IIb	3-(Cyclohexenyl-3')-propine-1-ol-3	88—85 (3)	1.5035	0.9818	49.60	49.28	79.61, 79.53	9.00, 9.13	$C_9H_{12}O$	79.41	8.82
IIIa	Acetate of 3-(6'-methylchclohexenyl-3')-propine-1-ol-3	M.p. 42—43	—	—	—	—	75.18, 75.28	8.27, 8.51	$C_{12}H_{16}O_2$	75.00	8.33
IIIb	Acetate of 3-(cyclohexenyl-3')-propine-1-ol-3	87 (2.5)	1.4820	1.0165	49.83	49.98	74.32	7.74	$C_{11}H_{14}O_2$	74.15	7.87
IVa	3-(6'-Methylcyclohexenyl-3')-propene-1-ol-3	71—72 (1)	1.4920	0.9555	46.89	46.77	79.20, 79.09	10.45, 10.50	$C_{10}H_{16}O$	78.94	10.52
IVb	3-(Cyclohexenyl-3')-propene-1-ol-3	90—91 (6)	1.4930	0.9591	41.76	42.15	78.08, 78.19	10.42, 10.40	$C_9H_{14}O$	78.26	10.14
Va	Acetate of 3-(6'-methylcyclohexenyl-3')-propene-1-ol-3	76—77 (1)	1.4702	—	—	—	74.01, 74.19	9.40, 9.46	$C_{12}H_{18}O_2$	74.23	9.28
Vb	Acetate of 3-(cyclohexenyl-3')-propene-1-ol-3	76—78 (3)	1.4700	—	—	—	73.48, 73.20	9.24, 9.15	$C_{11}H_{16}O_2$	73.33	8.88
VIa	3-(6'-Methylcyclohexanyl)-propanol-3	66—67 (1)	1.4654	—	—	—	77.00, 76.96	12.56, 12.48	$C_{10}H_{20}O$	76.92	12.82
VIb	3-cyclohexanylpropanol-3	82—84 (5)	1.4615	0.9140	42.77	43.08	75.79, 75.89	12.54, 12.60	$C_9H_{18}O$	76.05	12.67
VIIa	Acetate of 3-(6'-methylcyclohexanyl)-propanol-3	72—73 (1)	1.4492	—	—	—	72.92, 73.01	11.47, 11.30	$C_{12}H_{22}O_2$	72.72	11.11
VIIb	Acetate of 3-cyclohexanylpropanol-3	70—72 (3)	1.4508	—	—	—	69.70, 69.54	11.57, 11.43	$C_{11}H_{20}O_2$	69.76	11.62
VIIIa	3-(6'-Methylcyclohexenyl-3')-propanone-2-ol-3	M.p. 57—58	1.4870	—	—	—	71.35, 71.25	9.68, 9.70	$C_{10}H_{16}O_2$	71.43	9.52
VIIIb	3-(Cyclohexenyl-3')-propanone-2-ol-3	95—96 (3)	1.4960	1.0644	42.26	42.63	70.21, 70.04	9.28, 9.46	$C_9H_{14}O_2$	70.13	9.09
IXa	3-(6'-Methylcyclohexanyl)-propene-2	63—64 (13)	1.4560	—	—	—	86.67, 86.64	12.80, 12.90	$C_{10}H_{18}$	86.95	13.04
IXb	3-Cyclohexanylpropene-2	65—67 (15)	1.4545	—	—	—	87.21, 87.09	12.82, 12.68	C_9H_{16}	87.10	12.90
Xa	1-Methyl-2-propycyclohexane	62—63 (13)	1.4438	—	—	—	85.42, 85.51	14.01, 13.98	$C_{10}H_{20}$	85.71	14.28
Xb	Cyclohexylpropane	60—61 (13)	1.4420	—	—	—	85.40, 85.48	14.00, 14.12	C_9H_{18}	85.71	14.28
XIa	Di-1-(c'-Methylcyclohexenyl-3')-propenyl-2-ether	160—161 (1)	1.5017	0.9495	89.23	88.94	83.62, 83.88	10.66, 10.71	$C_{20}H_{30}O$	83.91	10.49
XIb	Di-1-(cyclohexenyl-3')-propenyl-2-ether	156—157 (1.5)	1.5094	0.9568	79.59	79.97	83.67, 83.47	10.24, 10.08	$C_{18}H_{26}O$	83.72	10.07
XIIa	Di-1-(2'-methylcyclohexenyl)-propyl ether	154 (1)	1.4754	—	—	—	81.21, 81.26	12.61, 12.80	$C_{20}H_{38}O$	81.63	12.89
XIIb	D-1-(cyclohexenyl)-propyl ether	156 (3)	1.4818	—	—	—	81.02, 81.22	13.01, 12.91	$C_{18}H_{34}O$	81.20	12.78
XIIIa	3-(6'-Methylcyclohexenylene-3')-propine-1	84 (17)	1.5170	0.9251	43.28	43.24	90.74, 90.62	9.11, 9.22	$C_{10}H_{12}$	90.91	9.09
XIIIb	3-(Cyclohexenylene-3')-propine-1	75—76 (14)	1.5184	0.9332	38.75	38.62	91.20, 91.14	8.32, 8.55	C_9H_{10}	91.52	8.47
XIVa	3-(6'-Methylcyclohexenylene-3')-propene-1	75 (17)	1.5055	0.8820	44.94	44.78	89.32, 89.25	10.44, 10.56	$C_{10}H_{14}$	89.55	10.45
XIVb	3-(cyclohexenylene-3')-propene-1	65—67 (15)	1.5075	0.8920	39.79	40.16	89.67, 89.74	10.04, 10.23	C_9H_{12}	90.00	10.00

by an investigation of their infrared spectra. Thus the structure of compound (XIVb) results from the presence in it of an absorption band in the 1600 cm^{-1} region, characteristic of conjugated double bonds, and an absorption band at 1653 cm^{-1}, characteristic of an isolated double bond in a Δ^3-cyclohexene ring.

The unsaturated hydrocarbons (XIII) obtained were converted by selective hydrogenation in the presence of $Pd/CaCO_3$ into hydrocarbons (XIV), further hydrogenation of which led to the saturated hydrocarbons (X). The properties of the secondary acetylene alcohols of the Δ^3-cyclohexene series we obtained are given in the Table.

EXPERIMENTAL

Condensation of Δ^3-hexahydrotoluylaldehyde with acetylene. A rapid current of acetylene was passed into a solution of 4.5 g of sodium metal in 400 ml of liquid ammonia with vigorous stirring at a temperature of -65 to -70°, until the blue color of the solution had disappeared. A solution of 25 g of aldehyde (I) (m.p. 65° at 15 mm, n_D^{20} 1.4652) in 50 ml of dimethoxymethane was added dropwise at thistemperature to the sodium acetylide in 20 min., without stopping the current of acetylene or the stirrer. The feed of acetylene (with stirring) was continued for a further 3 hours at -70° and 2 hours at -35 to -40°. The reaction mixture was decomposed with cold, acidified water. The product was extracted with ether, washed with water, dried with Na_2SO_4 and distilled under vacuum. We obtained 18.4 g of acetylene alcohol (IIa).

Acetylation. (IIIa). A solution of 18.4 g of acetylene alcohol (IIa) and 5.5 ml of acetyl chloride in 100 ml of anhydrous benzene were heated in the presence of 0.9 g of magnesium metal for 6 hours with vigorous stirring. The excess acetyl chloride and benzene were driven off under vacuum. 50 ml of water was added to the residue, the magnesium was filtered, the acidified solution was extracted with ether, dried with magnesium sulfate and the ether was distilled. The yield was 4.6 g of acetate (IIIa); the m.p. was 38-41° (from petroleum ether).

Selective hydrogenation. a) We hydrogenated 23 g of acetylene alcohol (IIa) in methyl alcohol with palladium catalyst on $CaCO_3$. In 3 hours, 3.42 liters of hydrogen were absorbed, corresponding to the hydrogenation of one bond. The catalyst was filtered, the solvent was distilled and the hydrogenation product was distilled under vacuum. We obtained 20 g of alcohol (IVa).

b) We hydrogenated 5.7 g of alcohol (IVa) in methyl alcohol with palladium catalyst in $CaCO_3$. In 2 hours, 0.84 liter of hydrogen was absorbed. The catalyst was filtered, the solvent was driven off and the hydrogenation product was distilled under vacuum. We obtained 4.5 g of saturated alcohol (VIa).

Hydration. We added 10 g of acetylene alcohol (IIa) at 60° to a solution of 4 g of mercury sulfate and 4 ml of sulfuric acid in 400 ml of water. The mixture was heated for 6 hours and extracted with ether; the extract was washed with water, dried with sodium sulfate and distilled under vacuum. We obtained 6.3 g of ketol (VIIIa) (b.p. 89° at 1 mm, n_D^{20} 1.4870), which crystallized out in the receiving flask and had an m.p. of 55-57° (from ether).

Dehydration of alcohol (VI) with potassium bisulfate. A mixture of 10 g of alcohol (VIa) and 2.5 g of baked potassium bisulfate powder was heated under vacuum for 1 hour at 180-190°. At the end of heating, the vacuum was increased and the product was distilled. We obtained 5.4 g of unsaturated hydrocarbon (IXa).

Hydrogenation of hydrocarbon (IX). We hydrogenated 3.5 g of unsaturated hydrocarbon (IXa) in 25 ml of methanol with Pd catalyst. In 1 hour, 0.6 liter of hydrogen was absorbed. The catalyst was filtered, the solvent was distilled and the hydrogenation product was distilled under vacuum. We obtained 2.1 g of saturated hydrocarbon (Xa).

Dehydration of alcohol (IV) with potassium bisulfate. A mixture of 6 g of alcohol (IVa) and 1.5 g of baked potassium bisulfate powder was heated under vacuum for 30 minutes at 175-180°. At the end of heating, the vacuum was increased and the product was distilled. We obtained 4.2 g of ether (XIa).

Hydrogenation of ether (XI). We hydrogenated 7 g of unsaturated ether (XIa) in 50 ml of methanol with a Pd catalyst. In 2 hours, 2.2 liters of hydrogen were absorbed. The catalyst was filtered, the solvent was driven off and the hydrogenation product was distilled under vacuum. We obtained 4.8 g of saturated ether (XIIa).

Dehydration of alcohol (II) by phosphorus oxychloride. We heated a mixture of 19.5 g of alcohol (IIa), 120 ml of pyridine and 6 ml of phosphorus oxychloride for 6 hours at a bath temperature of 130°. A further 6 ml of phosphorus oxychloride was added after 2 and 4 hours. The mixture was allowed to stand overnight and the excess pyridine was distilled under vacuum. The residue was cooled to room temperature, decomposed with ice water, extracted with ether and dried over sodium sulfate. The ether extract was shaken with activated carbon, the carbon was filtered, the solvent was driven off and the product was distilled under vacuum. We obtained 12.7 g of unsaturated hydrocarbon (XIIIa).

Selective hydrogenation of hydrocarbon (XIII). We hydrogenated 10 g of hydrocarbon (XIIIa) in methanol with Pd catalyst. In 3 hours, 1.7 liters of hydrogen were absorbed. The catalyst was filtered, the solvent was driven off and the product was distilled under vacuum. We obtained 5.6 g of unsaturated hydrocarbon (XIVa).

Dehydration of alcohol (IV) with phosphorus oxychloride. A mixture of 17 g of alcohol (IVa), 120 ml of pyridine and 5 ml of phosphorus oxychloride was heated for 6 hours at a bath temperature of 150°. A further 5 ml of phosphorux oxychloride was added after 2 and 4 hours. The mixture was allowed to stand overnight and the excess pyridine was distilled under vacuum. The residue was cooled to room temperature, decomposed with ice water, extracted with ether and dried over sodium sulfate. The solvent was driven off and the product was distilled under vacuum. We obtained 4.6 g of hydrocarbon (XIVa).

SUMMARY

By condensation of acetylene with Δ^3-cyclohexenol and 2-methyl-Δ^3-cyclohexenol the corresponding acetylene alcohols were synthesized, and their selective and exhaustive hydrogenation, hydration and dehydration were investigated. The latter reaction was investigated in detail under different conditions, not only with respect to secondary acetylene alcohols but also to the products of their selective and exhaustive hydrogenation.

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All abbreviations of periodicals in the above bibliography are letter-by-letter transliterations of the abbreviations as given in the original Russian journal. *Some or all of this periodical literature may well be available in English translation.* A complete list of the cover-to-cover English translations appears at the back of this issue.

STUDIES IN THE FIELD OF AMINES AND AMMONIUM COMPOUNDS

XIV. ALKALINE HYDROLYSIS OF AMMONIUM SALTS CONTAINING AN ALKOXYMETHYL GROUP IN δ-POSITION OF A β, γ-UNSATURATED RADICAL

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It was shown in preceding communications [1, 2] that quaternary ammonium salts containing a β,γ-unsaturated radical are easily cleaved with aqueous alkali with the formation of unsaturated compounds with conjugated double bonds.

In the present work, in order to study the effects of an electron acceptor group on the reaction with aqueous alkali, we extended our investigations to quaternary ammonium salts containing an alkoxymethyl group in the δ-position of the β, γ-unsaturated radical. For comparing the ease of radical cleavage, we have also studied quaternary ammonium salts containing two β, γ-unsaturated radicals. The results of the reaction of all these ammonium salts with aqueous alkali are given in the table. Cleavage of the salts occurs quite smoothly at the reaction mixture temperature of 90-105°.

It has been already shown [1] that the alkaline cleavage of quaternary ammonium salts containing a 3-chloro-2-butenyl radical leads to the formation, along with the simple cleavage product, of the reaction product of dehydrochlorination-cleavage, i.e., of chloroprene and vinylacetylene. Consequently, in the case of salts with a 3-chloro-5-methoxy-2-pentenyl radical (cf. expts. No. 2, 3, 6, and 9 in the table), one could expect the formation of two nitrogen-free products in agreement with the scheme:

$$R_3\overset{+}{N}-CH_2-CH=CCl-CH_2-CH_2OCH_3 \xrightarrow{\bar{O}H} \begin{cases} \rightarrow CH_2=CH-CCl=CH-CH_2OCH_3 \\ \rightarrow HC\equiv C-CH=CH-CH_2OCH_3 \\ \qquad\qquad \text{or} \\ \rightarrow CH_2=CH-C\equiv C-CH_2OCH_3 \end{cases}$$

This picture would have been modified if the presence of a methoxymethyl group influenced the reaction rate of the cleavage reaction and that of the dehydrochlorination-cleavage to different degrees.

As it can be seen in the table, in most of the cases (Nos. 2, 3, and 9), the only reaction product with alkali was the dehydrochlorination-cleavage product, i.e., 5-methoxy-1-penten-3-yne. Only in one case (No. 6), a small amount (13%) of 3-chloro-5-methoxy-1,3-pentadiene was obtained.

It follows that in the compounds studied, the effect of the methoxymethyl group on the reaction rate of dehydrochlorination-cleavage exceeds the effect exerted on the cleavage reaction rate.

The alkaline cleavage of ammonium salts containing two β, γ-unsaturated radicals (No. 5-10) can take place in two different ways:

$$(CH_3)_2\overset{+}{N}\begin{matrix} R \\ R' \end{matrix} \xrightarrow{\bar{O}H} \begin{cases} \rightarrow (CH_3)_2-N-R + X \\ \rightarrow (CH_3)_2-N-R' + Y \end{cases}$$

Results of the Alkaline Cleavage of Quaternary Ammonium Salts Containing an Alkoxymethyl Group in δ-Position of a β, γ-Unsaturated Radical

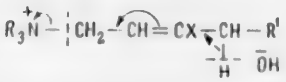
No.	Starting amine and halogen derivative for the preparation of the quaternary ammonium salt	Ionizable halide in the quaternary salt % found	% calc.	Cleavage products	Yield (in %)	M.p. of amine picrates
1	$(CH_3)_2N-CH_2-C\equiv C-CH_2-CH_2-O-CH_3$ [6]			$(CH_3)_3N$	86.7	—
	CH_3I	43.44	44.87	$CH_2=CH-C\equiv C-CH_2-O-CH_3$	86.7	—
2	$(CH_3)_2N-CH_2-CH=CCl-CH_2-CH_2-O-CH_3$ [6]			$(CH_3)_3N$	85.0	—
	CH_3I	39.46	39.74	$CH_2=CH-C\equiv C-CH_2-O-CH_3$	87.5	—
3	$(C_2H_5)_2N-CH_2-CH=CCl-CH_2-CH_2-O-CH_3$ [6]			$(C_2H_5)N-CH_3$	95.0	—
	CH_3I	36.1	36.54	$CH_2=CH-C\equiv C-CH_2-O-CH_3$	71.5	—
4	$(CH_3)_2N-CH_2-CH=\underset{\displaystyle CH_3}{\overset{\displaystyle |}{C}}-CH_2-CH_2-O-CH_3$			$(CH_3)_3N$	100	—
	CH_3I	42.13	42.47	$CH_2=CH-\underset{\displaystyle CH_3}{\overset{\displaystyle |}{C}}=CH-CH_2-O-CH_3$	75.4	—
5	$(CH_3)_2N-CH_2-C\equiv C-CH_2-CH_2-O-CH_3$	12.91	13.34	$(CH_3)_2N-CH_2-CH=CCl-CH_3$	33.0	120°
				$(CH_3)_2N-CH_2-C\equiv C-CH_3$	33.0	120
	$CH_3-CCl=CH-CH_2Cl$			$CH_2=CH-C\equiv C-CH_2-O-CH_3$	68.0	—
6	$(CH_3)_2N-CH_2-CH=CCl-CH_2-CH_2-O-CH_3$	11.99	11.73	$(CH_3)_2N-CH_2-CH=CCl-CH_3$	21.8	120
				$(CH_3)_2N-CH_2-C\equiv C-CH_3$	62.8	120
	$CH_3-CCl=CH-CH_2Cl$			$CH_2=CH-CCl=CH-CH_2-O-CH_3$	12.8	—
				$CH_2=CH-C\equiv C-CH_2-O-CH_3$	62.8	—
7	$(C_2H_5)_2N-CH_2-CH=CH-CH_3$			$(C_2H_5)_2N-CH_2-CH=CH-CH_3$	60.2	82—83

No.	Starting amine and halogen derivative for the preparation of the quaternary ammonium salt	Ionizable halide in the quaternary salt % found	% calc.	Cleavage products	Yield (in %)	M.p. of amine picrates
	$CH_3-O-CH_2-CH_2-\overset{\overset{CH_3}{|}}{C}=CH-CH_2-Cl$	14.0	12.88	$(C_2H_5)_2N-CH_2-CH=\overset{\overset{CH_3}{|}}{C}-CH_2-CH_2-O-CH_3$	30.5	189
				$CH_2=CH-\overset{\overset{CH_3}{|}}{C}=CH-CH_2-O-CH_3$	61.0	—
				$CH_2=CH-CH=CH_2$	26.0	—
8	$(CH_3)_2N-CH_2-CH=\overset{\overset{CH_3}{|}}{C}-CH_2-CH_2-O-CH_3$			$(CH_3)_2N-CH_2-CH=\overset{\overset{CH_3}{|}}{C}-CH_3$	47.7	102—103
	$(CH_3)_2-C=CH-CH_2-Cl$	13.53	13.57	$(CH_3)_2N-CH_2-CH=\overset{\overset{CH_3}{|}}{C}-CH_2-CH_2-O-CH_3$	21.4	88—89
				$CH_2=CH-\overset{\overset{CH_3}{|}}{C}=CH-CH_2-O-CH_3$	50.0	—
				$CH_2=CH-\overset{\overset{CH_3}{|}}{C}=CH_2$	20.0	—
9	$(CH_3)_2N-CH_2-CH=\overset{\overset{CH_3}{|}}{C}-CH_2-CH_2-O-CH_3$	10.66	10.88	$(CH_3)_2N-CH_2-CH=\overset{\overset{CH_3}{|}}{C}-CH_2-CH_2-O-CH_3$	73.4	88—89
	$CH_3-O-CH_2-CH_2-CCl=CH-CH_2Cl$			$CH_2=CH-C\equiv C-CH_2-O-CH_3$	74.5	—
10	$(CH_3)_2N-CH_2-C\equiv C-CH_3$ [1]	13.33	14.45	$(CH_3)_2N-CH_2-CH=\overset{\overset{CH_3}{|}}{C}-CH_2-CH_2-O-CH_3$	74.0	88—89
	$CH_3-O-CH_2-CH_2-\overset{\overset{CH_3}{|}}{C}=CH-CH_2Cl$			$CH_2=CH-C\equiv C-H$	—	—

The yields of the nitrogen-free products X and Y will depend on the relative cleavage rate of the corresponding β, γ-unsaturated radical. The table shows that the 5-methoxy-2-pentenyl radical is the one which is split with the greatest ease under the influence of aqueous alkali. According to their readiness to undergo cleavage, the radicals can be placed in the following sequence:

$$-CH_2-C\equiv C-CH_2-CH_2OCH_3 > -CH_2-CH=CCl-CH_2-CH_2OCH_3 > -CH_2-C\equiv C-CH_3 > -CH_2-CH=C(CH_3)-CH_2-CH_2OCH_3 > -CH_2-CH=CH-CH_3 > -CH_2-CH=C(CH_3)-CH_3$$

The results obtained are in agreement with the assumption that the stage which determines the reaction rate of the alkaline cleavage of quaternary ammonium salts is that of the removal of a proton from the δ-position of the β, γ-unsaturated radical.



The comparative ease with which the proton is split off will be naturally increased by the introduction of an electron-acceptor substituent R^1.

The greater ease of proton removal in 5-methoxy-2-pentenyl, and 2-butenyl radicals as compared to 3-methyl-5-methoxy-2-pentenyl radical is obviously explained by the stronger electron-acceptor influence of the triple bond in comparison with a double bond, as well as by the presence of an electron-donor methyl group in the latter radical.

With the exception of 1-dimethylamino-3-methyl-5-methoxy-2-pentene, all the other amines used as starting materials for the preparation of ammonium salts have been synthesized according to the references following the names of the amines in the table. The structure of 3-methyl-5-methoxy-1,3-pentadiene was determined by ozonolysis which gave methoxyacetic acid and formic acid. 5-Methoxy-1-penten-3-yne [3], and 3-chloro-5-methoxy-1,3-pentadiene are described in [4]. The constants of these compounds as determined by us coincided with those given in the literature. 1-Chloro-3-methyl-5-methoxy-2-pentene, which we needed for our syntheses, was prepared by the chloromethylation of isoprene as described by Pudovik [5] with some modifications (use of Neozone "D", lower reaction temperature, longer duration of the reaction), which allowed us to raise the yield of the chloroether from 30 to 58%.

EXPERIMENTAL

1-Dimethylamino-3-methyl-5-methoxy-2-pentene. Dimethylamine was passed through a solution of 74.25 g of 1-chloro-3-methyl-5-methoxy-2-pentene in 300 ml of dry ether until 64 g was absorbed. The mixture was allowed to stand for 24 hr; it was then diluted with water and extracted with ether. The ethereal extract was acidified with the calculated amount of hydrochloric acid needed for the separation of the amine from unreacted chloroether. Making the hydrochloric acid solution alkaline gave 56.4 g (71.7%) of the amine.

M. p. 71-72° (10 mm), d_4^{20} 0.8596, n_D^{20} 1.4460, MR_D 48.69. calc. 48.89.

Found %: N 8.88. $C_9H_{19}ON$. Calculated %: N 8.91.

Its picrate melted at 88-89°.

The alkaline cleavage of all the salts mentioned in table was carried out by heating with 20-25% aqueous alkali at 90-105°. When a salt contained a chlorine atom, the amount of alkali added was 3 moles; in the other cases, it was 2 moles. The cleavage products were removed as soon as formed by continuous distillation from the reaction mixture. The gaseous products were collected in a coil receiver cooled to -80°. The volatile amines were estimated by titration of the aqueous and upper layers of distillates. Neutral products and amines were separated from the distillate in the usual way, and were distilled after removal of solvents.

The amines were identified by mixed melting point determination of their picrates with authentic samples.

3-Methyl-5-methoxy-1,3-pentadiene. A mixture of 60.2 g of trimethyl-5-methoxy-2-pentenyl ammonium iodide and 24 g of potassium hydroxide in 60 ml of water was heated on a sand-bath to 105°. The temperature was raised to 120° in order to distill the reaction products. After the usual treatment, 16 g (71.4%) of the required product was obtained.

M. p. 131-132° (680 mm), d_4^{20} 0.8389, n_D^{20} 1.4620, MR_D 36.70; calc. 36.12.

Found %: C 75.19; H 10.85. $C_7H_{12}O$. Calculated %: C 75.0; H 10.71.

During hydrolysis, 0.2 moles (100%) of trimethylamine was formed.

Ozonolysis. A stream of ozonized oxygen (5% ozone) was passed at the rate of 7.5 liters/hr for 20 hr through a solution of 10 g of the diene in 40 ml of dry chloroform. After removal of the solvent by distillation, the reaction mixture was shaken for 5 hr with 65 ml of 10% hydrogen peroxide. The mixture was then extracted with ether, and the ethereal extract dried. A sample of the ethereal extract gave a white precipitate with mercuric chloride solution, showing that formic acid was present. Distillation of the ethereal extract gave methoxyacetic acid (b.p. 90-100° at 65 mm), which was converted into its silver salt.

Found %: Ag 54.80. $C_3H_5O_3Ag$. Calculated %: Ag 54.82.

SUMMARY

Quaternary ammonium salts containing an alkoxymethyl group in the δ-position of a β,γ-unsaturated radical are easily cleaved by aqueous alkali with the formation of unsaturated compounds containing the alkoxymethyl group and conjugated double bonds.

In ammonium compounds containing chlorine in the γ-position of a β,γ-unsaturated radical, the influence of the methoxymethyl group on the rate of dehydrochlorination-cleavage is stronger that the one it exerts on the rate of cleavage unaccompanied by dehydrochlorination.

A sequence of radicals according to the relative ease of their cleavage has been established on the basis of the results of the alkaline cleavage of ammonium compounds containing two β,γ-unsaturated radicals capable to undergo cleavage.

1-Dimethylamino-3-methyl-5-methoxy-2-pentene, and 3-methyl-5-methoxy-1,3-pentadiene are described for the first time.

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CHLOROMETHYLATION OF ACETOPHENONE AND 2-ACETOTHIENONE IN THE PRESENCE OF AN EXCESS OF ALUMINUM CHLORIDE

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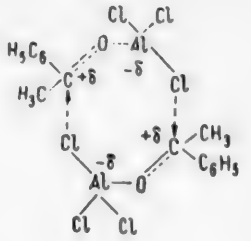
In 1930, Woolfe [1] patented a method for the introduction of a second acyl group in acyl-m-xylenes by the action of acyl chlorides in the presence of 3 moles of aluminum chloride. Recently, an analogous method was used by Pearson et al. [2] for the halogenation of acetophenone. Under such conditions, the halogen enters only the ring; the authors explain this effect by the blocking of the sidechain due to the formation of a stable hybrid complex with a dimeric cyclic structure.

We showed in 1959 [3] that Pearson's blocking method may be used for the introduction of bromine in the ring of 2-acetothienone. The reaction products in this case were 4-boromo-2-acetothienone, and a little of 4,5-dibromo-2-acetothienone; 5-boromo-2-acetothienone was not detected. At the same time [4], by using an excess of aluminum chloride, it became possible to introduce a second acyl group in the ring of certain monoacetylated thiophene homologs.



In the light of these facts, it appeared interesting to study the possibility of utilizing an excess of aluminum chloride for the nuclear chloromethylation of 2-acetothionone and acetophenone. Similarly to halogenation and acylation, chloromethylation belongs to electrophilic substitution reactions [5].

This is only a limited number of data in the literature on the chloromethylation of aldehydes and ketones. The chloromethylation of salicylic, o-homosalicylic [6], and anisic aldehydes [7] has been described; the presence of a hydroxyl group in the first two cases, and that of a methoxyl group in the latter case, considerably favors the reaction, whereas the negative group hinders this process. In 1936 [8], a number of chloromethyl derivatives of ketones of the fatty series have been prepared with a 30-35% yield; later [9], the chloromethylation of acetone was achieved, and chloromethyl derivatives of acetaldehyde and methyl ethyl ketone were obtained in small yields. Nuclear chloromethylation of aliphatic-aromatic ketones could be achieved only in cases when the aryl radical was substituted with at least two alkyl groups [10]; under similar conditions acetophenone and benzophenone [10] resisted nuclear chloromethylation. M. N. Tilichenko and V. A. Popova [11] who were the first to use boron fluoride etherate as a catalyst for chloromethylation succeeded to chloromethylate acetophenone and propiophenone in the side-chain. However, the data obtained by these authors for acetophenone are doubtful, as the compound they isolated melted 11° below the reported m.p. of β-chloropropiophenone, and was not analyzed.

The nuclear chloromethylation of aldehydes and ketones of the thiophene series has not been reported. Hartough [12] in this monography, with a reference to an unpublished work by the same author, only indicates that

2-acetothienone may undergo chloromethylation in the side chain with the formation of β-chloroethyl-2-thienyl ketone.*

Chloromethylation of acetophenone with the help of chloromethyl ether in the presence of 2.5 moles of anhydrous aluminum chloride and in the absence of a solvent led us to m-(chloromethyl)-acetophenone, which has not yet been described in the literature. The yield of the reaction was 39% with respect to the starting material and 54% with respect of the acetophenone which entered the reaction. The structure of the new compound was proved by its oxidation to isophthalic acid, the identity of which was confirmed by the preparation of the corresponding dimethyl ester, and by the synthesis of the nitrophenylhydrazone and the phthalimide derivative.

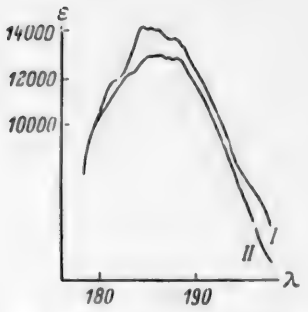


Fig. 1. Ultraviolet spectra of the diamides of α-methylglutaric acids from different sources (in water). I) From the products of reductive desulfurization, λ_{max} 185 mμ (ε 14.000); II) synthetic product, λ_{max} 185 mμ (ε 13.000).

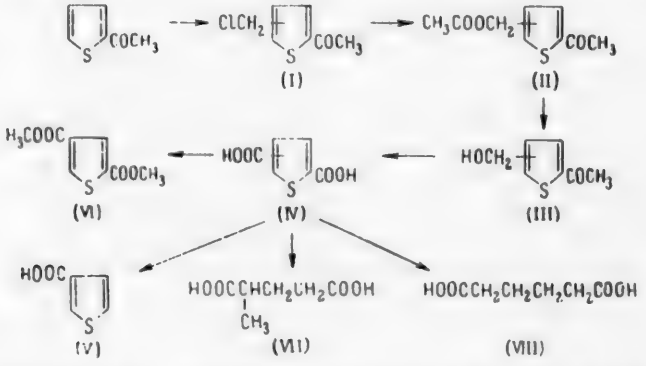
Under similar conditions, 2-acetothienone gave a mixture of nuclear chloromethylation products, viz., 4-(chloromethyl)- and 5-(chloromethyl)-2-acetothienones (I).

While carrying out chloromethylation reactions, we observed the considerable "sensitivity" of this reaction to changes in any of the conditions of the process, a fact which has been already described in the literature [13]. The chloromethylation of 2-acetothienone showed a particular "sensitivity" toward temperature changes: a small rise in temperature during the addition of chloromethyl ether led to a complete charring of the reaction mass. In the case of acetophenone, the use of 3 moles of aluminum chloride instead of 2.5 moles at a given temperature also provoked charring; lowering of the temperature in this case led to the complete recovery of the starting acetophenone.

While studying the action of sodium acetate on the chloromethylation product of 2-acetothienone (I), we noticed that the chlorine atom was less reactive to this reagent than in the case of 2,5-bis(chloromethyl)-thiophene [14], and 3,4-bis(chloromethyl)-2,5-dimethylthiophene [15]. When this reaction was carried out at 60°, the starting ketone (I) was recovered quantitatively. Substitution could be effected only at the boiling temperature of acetic acid.

The use of aluminum chloride as a catalyst in chloromethylation reactions of aromatic compounds often leads to the formation of diarylmethane derivatives as by-products[16]. Both the ketones under investigation were partly transformed during chloromethylation to diacetyl derivatives of diphenylmethane and dithienylmethane. These derivatives were isolated and characterized; apparently they are 3,3'-diacetyldiphenylmethane, and 5,5'-diacetyl-3,3'-dithienylmethane. The structure of these compounds will be proved in the next communication.

In order to determine the composition of the mixture obtained by chloromethylation of 2-acetothienone, the product initially obtained (I) was converted into a mixture of 2,4- and 2,5-thiophenedicarboxylic acids (IV) through the corresponding acetoxymethyl-2-acetothienones (II) and hydroxymethyl-2-acetothienones (III).



* After the present work was submitted for publication, communications concerning the chloromethylation of 2-acetothienone [26], and 2-acetylselenophenone [27] under usual conditions appeared in the literature. According to these authors they obtained in both cases only the 5-chloromethyl derivatives of the mentioned ketones.

Decarboxylation of the mixture of thiophenedicarboxylic acids (IV) gave thiophene-3-carboxylic acid (V). This allowed us observe the presence of thiophene-2,4-dicarboxylic acid in the mixture of acids (IV). However, as the decarboxylation reaction usually does not proceed with a quantitative yield, we were unable to arrive at a conclusion concerning the amount of thiophene-2,4-dicarboxylic acid in the acid mixture (IV). Therefore, this mixture (IV) was submitted to reductive desulfurization with Raney nickel which led to a mixture of α-methylglutaric acid (VII) (from thiophene-2,4-dicarboxylic acid), and adipic acid (VIII) (from thiophene-2,5-dicarboxylic acid). These acids were separated from each other by treating the mixture with the minimum amount of cold ether in which (VII) was more soluble than (VIII). The product obtained from the ethereal solution melted at 71-72° (from benzene).

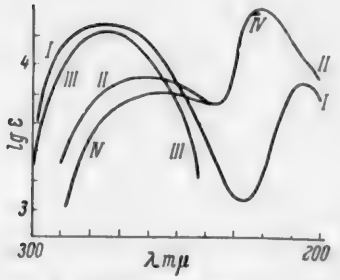


Fig. 2. Ultraviolet spectra of the dimethyl esters of thiophene 2,4- and 2,5-dicarboxylic acids and their mixture (in alcohol). I) Dimethyl ester of thiophene-2,5-dicarboxylic acid (Institute of Organic Chemistry, Academy of Sciences, USSR): λ_{max} 278 mμ (log ε 4.27), λ_{max} 206 mμ (log ε 3.88); II) dimethyl ester of the thiophene dicarboxylic acid isolated by the authors from the mixture: λ_{max} 256-266 mμ (log ε 3.91, λ_{max} 220 mμ (log ε 4.43; III) dimethyl ester of thiophene-2,5-dicarboxylic acid (Hopff and Crone): λ_{max} 268-278 mμ (log ε 4.228); IV) dimethyl ester of thiophene-2,4-dicarboxylic acid (Hopff and Crone): λ_{max} 256-257 mμ (log ε 3.812), λ_{max} 220 mμ (log ε 4.412).

Reported m.p. [17] for α-methylglutaric acid: 77-78°. This discrepancy prompted us to carry out the synthesis of α-methylglutaric acid [17]; the product obtained was converted via its dimethyl ester into its diamide (not described in the literature) which did not give a melting point depression with the diamide of acid (VII) prepared by the reductive desulfurization as described above. The identity of the two diamides was confirmed also by their ultraviolet absorption spectra in water* (Fig. 1).

The part which did not dissolve in ether consisted of adipic acid, m.p. 151-152° in agreement with the literature data [18].

α-Methylglutaric acid represented aoout 70%, and adipic acid, about 30% of the mixture of the acids obtained.** We came to the same conclusion concerning the predominance of the 2,4-isomer in the mixture of thiophene carboxylic acids by studying their dimethyl esters.

Hopff and Crone [19] have recently shown that mixtures of the dimethyl esters of thiophene-2,4- and 2,5-dicarboxylic acids melt over a broad range between the melting points of the two esters, the melting point of the mixture depending nearly linearly on their composition. Moreover, these authors compared the ultraviolet absorption spectra of the dimethyl esters of thiophene-2,4- and 2,5-dicarboxylic acids and their mixtures.

As the dimethyl ether obtained from the mixture of thiophene dicarboxylic acids melted at 123-124°, one could assume that it corresponded to a mixture with a considerable predominance of the 2,4- isomer (reported m.p. for the dimethyl esters: 120-121° for thiophene-2,4-dicarboxylic acid [19], and 148.5-149.5° for thiophene-2,5-dicarboxylic acid [14, 20].

A comparison of the ultraviolet absorption spectrum of the product with m.p. 123-124° with the spectra of the dimethyl esters of thiophene-2,4- and 2,5-dicarboxylic acids showed that this product consists of the dimethyl ester of thiophene-2,4-dicarboxylic acid contaminated with a few % of the 2,5-isomer (Fig. 2).

EXPERIMENTAL

Chloromethylation of acetophenone. Twenty four grams of anhydrous aluminum chloride was placed in a flask fitted with an efficient mechanical stirrer, reflux condenser, thermometer, and dropping funnel protected from moisture. Acetophenone (8.7 g) was introduced in the flask dropwise, while stirring, at a temperature not exceeding 60-70°, followed by 7.5 g of chloromethyl ether added dropwise at 40° over a period of 15 min. Then, the mixture was stirred at 65-70° for 6 hr, and left to stand overnight. On the next day, the thick black reaction product was

* The ultraviolet spectra were recorded in the optical laboratory of the Institute of Organic Chemistry, Academy of Sciences, USSR, by V. A. Petukhov, to whom the authors express their gratitude.

** It is obvious that these data do not necessarily correspond to the initial composition of the chloromethylation products, as the conversion of the latter to the corresponding acids was accomplished by a series of reactions.

poured on ice and extracted with ether thrice. The pooled ethereal extracts were washed with water, sodium bicarbonate solution, and water again, and finally dried over calcium chloride. The residue left after distillation of ether was submitted to vacuum distillation. The following fractions were isolated: Fraction I, b.p. 140° (10 mm), n_D^{20} 1.5360, 2.5 g; fraction II, b.p. 140-145° (10 mm), n_D^{20} 1.5578, 5.3 g. Fraction I consisted of recovered acetophenone (28.8% recovery). Repeated distillation of Fraction II gave 4.8 g of m-(chloromethyl)-acetophenone, b.p. 130-131° (7 mm), n_D^{20} 1.5580, yield: 54% w.r. to the acetophenone which has reacted, and 39.2% w.r. to the amount taken. An increase in the amount of chloromethyl ether did not lead to a better yield of chloromethylacetophenone.

Found %: C 64.24, 64.10; H 5.57, 5.58; Cl 21.25, 21.16. C_9H_9OCl. Calculated %: C 64.11; H 5.38; Cl 21.02.

2,4-Dinitrophenylhydrazone, m.p. 185-186° (from a mixture of alcohol and ethyl acetate).

Found %: N 15.84, 15.64. $C_{15}H_{13}O_4N_4Cl$. Calculated %: N 16.07.

A warm solution of potassium phthalimide (1.2 g) in 4 ml of dimethylformamide was treated with 1.1 g of m-(chloromethyl)-acetophenone. The mixture was heated on a boiling water-bath for 2.5 hr, cooled, and then treated with 6 ml of chloroform and 10 ml of water. The aqueous layer was separated, and extracted with chloroform. The pooled organic extracts were dried with anhydrous magnesium sulfate, and chloroform was distilled off. The residue thus obtained rapidly crystallized out, and was then recrystallized thrice from diluted alcohol. The m-(N-phthalimidomethyl)-acetophenone produced melted at 133-134°.

Found %: C 72.63, 72.88; H 4.55, 4.66; N 5.14, 5.04. $C_{17}H_{13}O_3N$. Calculated %: C 73.11; H 4.69; N 5.02.

In an analogous experiment on the chloromethylation of acetophenone, the mixture was heated at 50° for 8.5 hr. The ethereal extract yielded 3.5 g of recovered acetophenone, and 1.6 g of a substance which distilled with slight decomposition at 215-225° (4 mm), and melted at 79.5-80° (from diluted alcohol). The composition of this substance corresponded to that of diacetyldiphenylmethane.

Found %: C 81.04, 80.92; H 6.30, 6.25. $C_{17}H_{16}O_2$. Calculated %: C 80.92; H 6.39.

Isophthalic acid. A mixture of 2 g of m-(chloromethyl)-acetophenone, 45 ml of water, 15 ml of concentrated sulfuric acid, 45 ml of acetic acid, and 15 g of chromic anhydride was refluxed for 1.5 hr, and then allowed to cool to room temperature. The crystals, which separated out, were filtered off, repeatedly washed with cold water, and dried. Yield, 1.7 g (86.8%), m.p. 331-333°, reported m.p. [21], 330°.

Dimethyl ester of isophthalic acid. A suspension of 1.3 g of isophthalic acid in 150 ml of absolute ether was treated dropwise with an ethereal solution of diazomethane (from 5.3 g of nitrosomethylurea). After evolution of nitrogen has stopped, the mixture was boiled until practically all the solid residue dissolved (30 min). The solution was filtered off, and completely freed from ether by distillation. The residue thus obtained crystallized upon cooling. Yield, 1.44 g (96%), m.p. 67.5-68.0° (from diluted alcohol), reported m.p. [21], 68°. The substance prepared in this experiment did not depress the melting point of an authentic sample of dimethyl isophthalate.

Chloromethylation of 2-acetothienone. Twelve grams of 2-acetothienone was added dropwise with constant stirring, and keeping the temperature below 50-60°, to 32 g of anhydrous aluminum chloride. The liquid mixture thus obtained was cooled, but not enough to provoke solidification (usually not below 3-5°). Ten grams of chloromethyl ether was added dropwise during 2-2.5 hr to the mixture cooled as indicated, at such a rate as to prevent its temperature from rising above 8-10°. The first few drops had to be added with special care, as they could provoke a sharp rise in temperature. The mixture was then stirred for 3 hr at 5-10°, and for 4-5 hr at room temperature, and was finally left to stand overnight. As chloromethyl ether was being added, the reaction mass gradually became more and more fluid, and its color changed from brown to pale pink. After removal from the cooling bath, it started to redden, and soon became deep crimson-colored. The mixture was worked up as described for the chloromethylation of acetophenone, and finally distilled in vacuum. The following fractions were obtained: Fraction I, b.p. 73-123° (4 mm), n_D^{20} 1.5680, 2.6 g; fraction II, b.p. 123-135° (4 mm), n_D^{20} 1.5827, 9.0 g; residue consisting in 2-3 g of tar. Fraction I consisted of recovered 2-acetothienone (21.6% recovery). Repeated distillation of fraction II gave 7.5 g of a mixture of chloromethyl-2-acetothienones (I), b.p. 129-132° (4 mm), 132.5-135° (6 mm), 146-149° (9 mm), n_D^{20} 1.5830, yield: 57.7% w.r. to the acetothienone which has reacted, and 45.2% w.r. to the total amount taken.

Found %: C 48.54, 48.33; H 4.05, 4.07. C_7H_7OSCl. Calculated %: C 48.13; H 4.04.

In one of the experiments on the chloromethylation of 2-acetothienone, a crystalline substance was formed in the residue remaining after distillation of ether. This substance melted at 128.5-129.5° after two recrystallizations from benzene and one from a mixture of petroleum ether and benzene; its analytical data were those of diacetyldithienylmethane.

Found %: C 59.14, 59.21; H 4.59, 4.67; S 23.87, 23.86. $C_{13}H_{12}O_2S_2$. Calculated %: C 59.06; H 4.58; S 24.25.

Acetoxymethyl-2-acetothienones (II). A mixture of 5.3 g of anhydrous sodium acetate, 23 ml glacial acetic acid, and 10.3 g of the mixture of chloromethylacetothienones was refluxed with stirring for 5 hr. Acetic acid was removed in vacuum as completely as possible, and the residue was treated with water to dissolve the sodium acetate. The resulting mixture was extracted with ether, the ethereal extract washed with water, sodium carbonate solution, water again, and finally dried over calcium chloride, and distilled in vacuum. Yield, 9.5 g (81%), b.p. 160-164° (9 mm), 150-154° (5 mm), n_D^{20} 1.5440. The substance gave a negative test for halogen.

Found %: C 54.32, 54.21; H 5.34, 5.11; S 16.19, 16.37. $C_9H_{10}O_3S$. Calculated %: C 54.52; H 5.08; S 16.57.

Hydroxymethyl-2-acetothienones (III) [22]. A solution of metallic sodium (0.17 g) in 60 ml of absolute alcohol was cooled to room temperature, and then treated with 9.5 g of the mixture of acetoxymethyl-2-acetothienones. The solution was allowed to stand at room temperature for 48 hr. Alcohol and ethyl acetate were removed by vacuum distillation, and the residue was treated with 0.4 g of ammonium chloride and 10 ml of absolute alcohol (odor of ammonia); the mixture was shaken for a few minutes, the precipitated sodium chloride filtered off, and washed with alcohol; finally, the alcohol was driven off in vacuum. The residual orange viscous oil consisting of a mixture of hydroxymethyl-2-acetothienones (about 8.2 g) was used in the oxidation experiment without further purification.

Thiophene dicarboxylic acids (IV). Oxidation of the mixture of hydroxymethyl-2-acetothienones (prepared from 12.4 g of acetoxymethyl-2-acetothienones) with 9.6 g of sodium hydroxide, 30 g of potassium permanganate, and 5.5 ml of 30% hydrogen peroxide [22] led to 5.7 g of a mixture of thiophene dicarboxylic acids. Yield, 52.9%. Neutralization equivalent, 86.04; theoretical equivalent, 86.08.

Dimethyl ester of thiophene-2,4-dicarboxylic acid (IV). Treatment of 1.2 g of the acids in 150 ml of absolute ether with diazomethane (from 4.6 g of nitrosomethylurea) led to a quantitative yield of a dimethyl ester, m.p. 118.5-121°, which melted at 123-124° after four recrystallizations from 60% alcohol. Its mixed melting point with the dimethyl ester of thiophene-2,5-dicarboxylic acid was 131-137°, or 136-142° depending on the content of thiophene-2,5-dicarboxylic acid dimethyl ester. Reported m.p. for the dimethyl ester of thiophene-2,4-dicarboxylic acid [19]: 120-121°; for the dimethyl ester of thiophene-2,5-dicarboxylic acid: 148.5-149.5°[14, 20].

Found %: C 47.92, 48.00; H 4.22, 4.26; S 15.86, 16.08. $C_8H_8O_4S$. Calculated %: C 47.99; H 4.03; S 16.01.

Decarboxylation of the mixture of thiophene dicarboxylic acids [23]. A powdered mixture of 3.9 g of thiophene carboxylic acids, and 0.3 g of copper bronze, intimately mixed with 8 ml of freshly distilled quinoline was placed in a flask fitted with a reflux condenser the upper part of which was connected to an eudiometer for the collection of gases evolved during the reaction. The contents of the flask were refluxed for 1 hr (evolution of gases has stopped after 40 min). The total volume of gas produced was 640 ml (86% CO_2 and 3% O_2), corresponding to 550 ml of carbon dioxide (theoretical amount for one carboxyl group, 510 ml). The mixture in the reaction flask was dissolved in ether, copper was filtered off, and quinoline was extracted with three portions of 10% hydrochloric acid. The thiophene carboxylic acid was then extracted with 1% alkali, the alkaline solution acidified, the precipitate formed filtered off, and the filtrate extracted with ether. The total amount of thiophene-3-carboxylic acid obtained was 1.3 g, m.p. 136-137° (from water). This substance did not depress the melting point of an authentic sample of thiophene-3-carboxylic acid prepared from 3-bromothiophene [24].

Reductive desulfurization of the mixture of thiophene dicarboxylic acids. Sodium hydroxide (3.2 g) was added to a flask containing 290 ml of water and 4.8 g of the thiophene dicarboxylic acids mixture; the contents of the flask were heated to 70°, and treated with 30 g of Raney nickel. The reaction mixture was stirred at 70° until the test for sulfur was negative (1 hr), and then for a further 1 hr. The catalyst was filtered off, and twice boiled with water (100 ml portions). The pooled filtrate and washings were distilled in vacuum to dryness. The residue was dissolved in 15 ml of water, and the solution acidified with hydrochloric acid, and extracted with ether thrice. The oily residue obtained after removal of ether by distillation crystallized upon standing in a vacuum dessicator; yield, 3.3 g; m.p. 62-110°. The mixture of acids was triturated in a beaker with three small portions of ether, and

the washings decanted. The residue left in the beaker consisted of 0.88 g of product (A), m.p. 148-150°; the ethereal washings gave upon evaporation of the solvent 2.22 g of product (B), m.p. 69-90°. Product (B) was triturated again with ether, the solvent decanted, product (A) was added to the residue, and the mixture was treated once again with ether. The final residue consisted of 0.88 g of adipic acid (VIII), m.p. 151-152° [from nitric acid (sp.gr. 1.4) or ethyl acetate] giving no m.p. depression when mixed with an authentic sample of adipic acid. The ethereal solution gave 2.04 g of α-methylglutaric acid (VII), m.p. 71-72° (from benzene). The mixed melting point of the latter substance with α-methylglutaric acid prepared from malonic ester [17], and melting at 75-76° was 70-75°.

Found %: C 49.25, 49.33; H 6.80, 6.92. $C_6H_{10}O_4$. Calculated %: C 49.31; H 6.90.

Neutralization equivalent of adipic acid, 72.46; that of α-methylglutaric acid, 75.21. Theoretical for both acids, 73.07.

Dimethyl ester of α-methylglutaric acid. Dimethyl α-methylglutarate was prepared from 3.9 g of synthetic α-methylglutaric acid [17] and an ethereal solution of diazomethane. Yield, 3.8 g (82%); b.p. 109-110° (20 mm), n_D^{20} 1.4260.

Found %: C 55.12, 54.87; H 8.08, 7.87. $C_8H_{14}O_4$. Calculated %: C 55.26; H 8.04.

In a similar way, 1.5 g of α-methylglutaric acid isolated from the products of reductive desulfurization was converted into its dimethyl ester. Yield, 72%, b.p. 109-115° (20 mm), n_D^{20} 1.4261.

α-Methylglutaric acid diamide. Dimethyl α-methylglutarate (1.74 g) prepared from the synthetic acid was added to 6 ml of concentrated aqueous ammonia saturated with gaseous ammonia at 0°; the flask was tightly closed and left to stand at room temperature, the mixture being periodically shaken. After 24 hr the separation of phases disappeared, and after 3 days the solution was reduced to a volume of 3 ml by distillation. Yield of the diamide, 1.4 g (99%), m.p. 151.5-152° (from isobutyl alcohol).

Found %: N 19.20, 18.97. $C_6H_{12}O_2N_2$. Calculated %: N 19.42.

A mixture of aqueous ammonia saturated with ammonia at 0° (5 ml), and 1.25 g of the dimethyl ester of α-methylglutaric acid (from the products of reductive desulfurization) was kept with occasional shaking for 4 days. The precipitate which separated out (0.02 g) was filtered off and dried. It melted at 220-221° and consisted of the diamide of adipic acid (reported m.p. [25], 220-221°). The filtrate was evaporated to a volume of about 2 ml. The resulting precipitate (0.7 g) melted at 151.5-152° after four recrystallizations from isobutyl alcohol; it gave no m.p. depression with an authentic sample of synthetic diamide. An additional 0.3 g of the diamide was obtained from the mother liquor. Total yield, 96.7%.

Found %: N 18.95, 19.21. $C_6H_{12}O_2N_2$. Calculated %: N 19.42.

SUMMARY

1. Nuclear methylation of acetophenone and 2-acetothienone was achieved by reaction with chloromethyl ether in the presence of 2.5 moles of anhydrous aluminum chloride in the absence of a solvent.

2. Chloromethylation of acetophenone gave m-(chloromethyl)-acetophenone, the structure of which was established by its conversion into isophthalic acid and dimethyl isophthalate.

3. Chloromethylation of 2-acetothienone led to a mixture containing 4- and 5-chloromethyl-2-acetothienones, in which the 4-isomer apparently predominated.

4. Reductive desulfurization of a mixture of thiophene 2,4- and 2,5-dicarboxylic acids prepared by the oxidation of a mixture of the chloromethyl derivatives of 2-acetothienone led to the formation of α-methylglutaric acid and adipic acid (yields, 70% and 30%, respectively).

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STUDIES IN THE FIELD OF SYNTHETIC DYES

XX. CYCLYZATION OF p,p'-DITOLYLAMINE TO A QUATERNARY LEPIDINIUM SALT, AND SOME REACTIONS OF THE LATTER

G. T. Pilyugin and B. M. Gutsulyak

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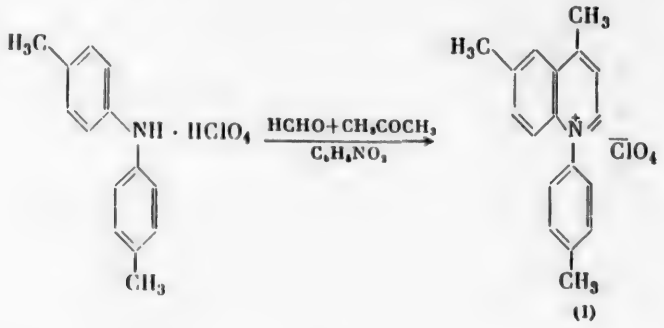
Translated from Zhurnal Obshchei Khimii,
Vol. 31, No. 2, pp. 623-626, February, 1961
Original article submitted February 22, 1960

It has been established during a study of N-aryl quaternary quinolinium salts and quinolinium derivatives that these compounds are more reactive than the corresponding alkyl-substituted compounds [1]. Aryl lepidinium salts have been less extensively studied than isomeric quinaldinium salts. By applying Beyer's reaction to secondary aromatic amines, we succeeded to prepare and investigate some aryl-substituted quaternary lepidinium salts. To increase the reaction rate and to improve the yields, we carried out this reaction with nitrobenzene as oxidizing agent [3].

In the present communication we describe the cyclyzation of p,p'-ditolylamine with acetone and formaldehyde in the presence of perchloric acid, and the conversion of the salt thus obtained into cyanine dyes.



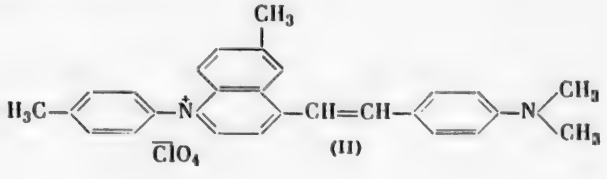
(I)

Experimental data show that the use of perchloric acid instead of hydrochloric acid leads to better yields of the quaternary salt. The salt obtained under these conditions, viz., N-p-tolyl-6-methyllepidinium perchlorate (I) is more soluble in water than 1-phenyllepidinium perchlorate.

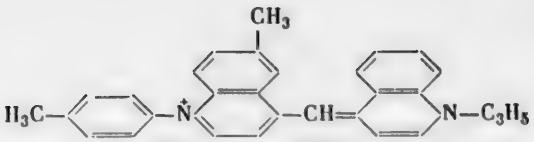
Condensation of the quaternary salt (I) with p-dimethylaminobenzaldehyde in acetic anhydride gave the styryl derivative (II) having the absorption maximum at 571 mμ.

Reaction of (I) with ethylquinolinium iodide in the presence of alkaline catalysts gave the cyanine derivative (III) having an unsymmetrical structure and displaying the absorption maximum at 598 mμ.

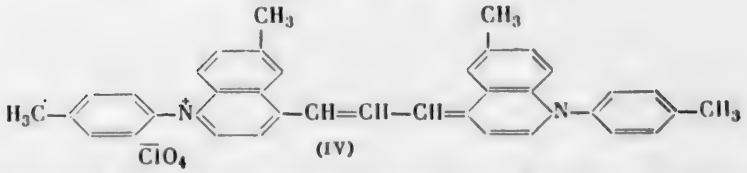
Condensation of the quaternary salt (I) with orthoformic ester in pyridine gave the symmetrical trimethinecyanine (IV) having the absorption maximum at 728 mμ.



(II)



(III)

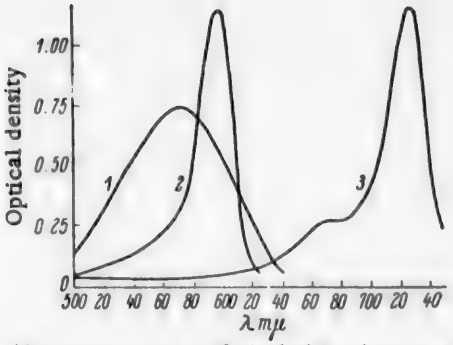


(IV)

The absorption spectra of the dyes under study were recorded in the visible part of the spectrum with the help of the recording spectrophotometer SF-2M (see graph).

EXPERIMENTAL

N-p-Tolyl-6-methyllepidinium perchlorate. Ten grams of p,p'-ditolylamine, 10 ml of water, 14 ml of 30% perchloric acid, 13 ml of nitrobenzene, and 32 ml of acetone were placed in a three-necked flask fitted with a mechanical stirrer, a reflux condenser, and a dropping funnel. The mixture was heated on a water-bath. When the bath temperature reached 100°, stirring was started, and 5 ml of 30% formaldehyde solution was introduced dropwise through the dropping funnel during 30 min. While the reaction was taking place, the condenser was cooled with ice-cold water. After all the amount of formaldehyde has been added, heating was continued for 7 hr with continuous stirring. After the reaction was over, the aqueous layer was decanted, and the brown tar remaining in the flask was repeatedly treated with small portions of boiling water, until the acidified aqueous washings stopped giving a white precipitate with a concentrated aqueous solution of potassium ferrocyanide, or a bright orange deposit with potassium bismith iodide. The combined aqueous extracts were boiled with activated charcoal, filtered and concentrated by evaporation in a porcelain dish (water-bath) to incipient crystallization of the quaternary salt. The long colorless needle crystals thus obtained were filtered off and recrystallized first from water, and then from alcohol, m.p. 154-155° (dec.). Yield, 8.1 g (46.6%). This product is rather easily soluble (better than 1-phenyllepidinium perchlorate) in water, acetone, alcohol, chloroform, pyridine, and quinoline, difficultly soluble in hydrocarbons, and practically insoluble in ether and carbon tetrachloride.



Absorption spectra of alcoholic solutions of dyes. 1) (N-p-tolyl-6-methylquinoline-4)-p-dimethylaminostyryl perchlorate; 2) N-p-tolyl-4-methylquinoline-4-(N-ethylquinoline-4)-monomethinecyanine perchlorate; 3) bis-(N-p-tolyl-6-methylquinoline-4)-trimethinecyanine perchlorate.

Found %: Cl 10.39, 10.24; N 4.16. $C_{18}H_{18}O_4NCl$. Calculated %: Cl 10.19; N 4.03.

N-p-Tolyl-6-methyllepidinium picrate. A saturated aqueous solution of picric acid was added dropwise to an aqueous solution of 2 g of N-p-tolyl-6-methyllepidinium perchlorate until it ceased to produce a turbidity. The mixture was left to stand overnight. The lemon-yellow precipitate, which separated out, was filtered off and recrystallized from a 1 : 1 mixture of alcohol and acetone. The fine lemon-yellow needle crystals of the picrate melted at 230-232° (dec.). Yield, 2.4 g (90%). This substance was easily soluble in acetone, and alcohol, more difficultly soluble in water, and insoluble in ether.

Found %: N 12.16, 11.92. $C_{24}H_{20}O_6N_4$. Calculated %: N 11.76.

(N-p-Tolyl-6-methylquinoline-4)-p-dimethylaminostyryl perchlorate (II). A mixture of 3.5 g of N-p-tolyl-6-methyllepidinium perchlorate, 2 g of p-dimethylaminobenzaldehyde, and 10 ml of acetic anhydride was gently

boiled for 15 min in a small flask fitted with a reflux condenser (paraffin bath). The reaction mixture was then allowed to stand for 24 hr. The fine crystals formed in the mixture were filtered off, and recrystallized from a mixture of alcohol and acetone. The fine greyish-green crystals of II melted at 248-249° (dec.). Yield, 3.06 g (63.4%). II was readily soluble in pyridine, quinoline, acetic anhydride, acetone, and chloroform, somewhat less soluble in alcohol, and practically insoluble in dioxane, hydrocarbons, carbon tetrachloride, water, and ether. The color of its alcoholic solution was violet.

Found %: Cl 7.38, 7.14; N 6.03. $C_{27}H_{27}O_4N_2Cl$. Calculated %: Cl 7.40; N 5.84.

N-p-Tolyl-6-methylquinoline-4-(N-ethylquinoline-4)-monomethinecyanine perchlorate (III). N-p-tolyl-6-methyllepidinium perchlorate (1.2 g), 1.5 g of N-ethylquinolinium iodide, 0.6 g of finely powdered anhydrous potassium carbonate, and 10 ml of absolute alcohol were mixed in a small flask and heated on a water-bath at 80° for 15 min. The reaction mixture was then poured into 200 ml of a dilute solution of sodium perchlorate The dye precipitated out as a violet product which was filtered off and recrystallized from aqueous alcohol, m.p. 149-150° (dec.). Yield, quantitative. III dissolved in the same solvents as the foregoing product, but considerably better. Its synthesis in the presence of alcoholic alkali gave a lower yield (63%).

Found %: Cl 7.15, 7.19; N 5.70. $C_{29}H_{27}O_4N_2Cl$. Calculated %: Cl 7.05; N 5.57.

Bis-(N-p-tolyl-6-methylquinoline-4)-trimethinecyanine perchlorate (IV). N-p-tolyl-6-methyllepidinium perchlorate (2.7 g), 2 ml of dry pyridine, and 1.2 ml of orthoformic ester were mixed in a small flask and gently boiled on a paraffin bath for 1 hr. The reaction mixture gradually turned green. The dye was precipitated with ether, filtered off, and washed with ether to the complete removal of pyridine. After recrystallization from acetone, IV appeared as a finely crystalline powder with metallic lustre, m.p. 300° (dec.). Yield, 0.7 g (34%). It was soluble in acetone, alcohols, pyridine, quinoline, and acetic anhydride, and insoluble in water, hydrocarbons, carbon tetrachloride, and ether.

Found %: Cl 5.80, 5.72; N 4.69. $C_{37}H_{33}O_4N_2Cl$. Calculated %: Cl 5.86; N 4.63.

SUMMARY

1. The quaternary salts N-p-tolyl-6-methyllepidinium perchlorate and picrate were prepared and characterized.

2. The following new dyes were synthesized from the mentioned perchlorate, and described: a) (N-p-tolyl-6-methylquinoline-4)-p-dimethylaminostyryl perchlorate, b) N-p-tolyl-6-methylquinoline-4-(N-ethylquinoline-4)-monomethinecyanine perchlorate, and c) bis-(N-p-tolyl-6-methylquinoline-4)-trimethinecyanine perchlorate.

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FORMYLATION OF Δ^2-PYRAZOLINE DERIVATIVES

E. E. Baroni and K. A. Kovyrzina

Translated from Zhurnal Obshchei Khimii, Vol. 31, No. 2,
pp. 627-628, February, 1961
Original article submitted February 29, 1960

Methods for introducing an aldehyde group into heterocyclic compounds are extremely limited. The Gattermann reaction has been found of some use [1], but it gives only slight yields and its conduct is associated with certain experimental difficulties. Direct formylation in a heterocyclic series was first achieved by King and Nord [2], using methylformanilide and phosphorus oxychloride as the formylation agent. Weston showed [3] that ethylformanilide can also be used for this purpose. In 1948 dimethylformamide was patented [4] as an effective agent for formylating aromatic tertiary amines. Tyson and Shaw [5], using dimethylformamide, prepared 3-indolyl aldehyde in 72% yield. This formylating agent differs from methylformanilide in its comparatively low cost and high formylation effectiveness. In recent years, by direct formylation of heterocycles with dimethylformamide it has been possible to introduce an aldehyde group into thiophene [6], into several derivatives of pyrazole [7], furan [8], and pyrrole [9].

We have carried out the formylation of 1,5-diphenyl-Δ^2-pyrazoline with dimethylformamide. Introduction of an aldehyde group into Δ^2-pyrazolines opens up new possibilities in the synthesis of luminescent compounds of the heterocyclic series. Direct formylation of Δ^2-pyrazolines with dimethylformamide is of practical interest owing to the simplicity of the reaction and the high yield. Formylation is best carried out with a six-fold excess of dimethylformamide at 95-100°. A higher temperature (125-130°), and also a smaller amount of amide, leads to low yields with formation of tarry products and even to charring.

EXPERIMENTAL

1,5-Diphenyl-3-formyl-Δ^2-pyrazoline. To 1,5-diphenylpyrazoline (5 g, 0.02 mole) and dimethylformamide (10 ml) at 75-85° with stirring over a period of 1 hour phosphorus oxychloride (4 ml) was added. Heating and stirring were then continued for 2 hours at 95-100°. The brownish, viscous oil was cooled to room temperature. On decomposing with ice, a greenish-yellow precipitate settled out, which was separated off and washed twice on the filter with a small amount of acetone. After recrystallizing from alcohol, yellow crystals were obtained with m.p. 105-106°, poorly soluble in ether, soluble in alcohol, acetone, and benzene. The benzene solution possessed an intense blue fluorescence. Yield 68%.

Found %: N 11.30, 11.15. $C_{16}H_{14}ON_2$. Calculated %: N 11.19.

Phenylhydrazone: m.p. 177° (decomp., from alcohol).

Found %: N 16.65, 16.62. $C_{22}H_{20}N_4$. Calculated %: N 16.47.

SUMMARY

Direct of formylation of 1,5-diphenyl-Δ^2-pyrazoline with dimethylformamide was achieved.

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CYANINE DYES CONTAINING FLUORINE

IX. CYANINE DYES FROM 5,6-(DIFLUOROMETHYLENE)-DIOXYBENZTHIAZOLE DERIVATIVES

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Institute of Organic Chemistry, Academy of Sciences, USSR
Translated from Zhurnal Obshchei Khimii, Vol. 31, No. 2,
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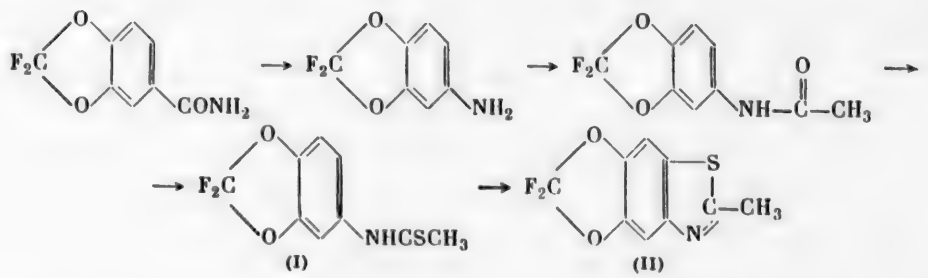
Original article submitted March 1, 1960

The cyanine dyes from 2-methyl-5,6-methylenedioxybenzthiazole and benzselenazole described [1] are photosensitizers for a silver halide emulsion. It was of interest to examine the effect of exchanging hydrogen atoms for fluorine in the methylenedioxy group on color and sensitizing properties of the dyes. Aromatic compounds containing a difluoromethylenedioxy group are not known in the literature. Recently, we described the synthesis of a piperonal analog obtained from difluoromethylene-3,4-dioxybenzoic acid [2].

As the starting point in the present work was chosen the amide of difluoromethylene-3,4-dioxybenzoic acid, which by a Hofmann reaction was converted into the amine and then via the acetamino compound—by a Jacobsen reaction—into the corresponding benzthiazole derivative, according to the scheme.

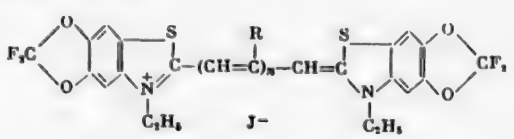


(I) (II)

The thioacetyl derivative (I) can be closed by oxidation into the 2-methyl-5,6- or the 6,7-difluoromethylenedioxybenzthiazole. As proof of the structure, the base obtained was converted by heating in a sealed tube with concentrated hydrochloric acid into 2-methyldioxybenzthiazole. The latter gave no melting point depression with the preparation submitted to us by A. I. Kiprianov and G. M. Lysak which they obtained by saponification of 2-methyl-5,6-dimethoxybenzthiazole with hydrobromic acid. Thus, on closing the thioacetyl derivative (I), 2-methyl-5,6-difluoromethylenedioxybenzthiazole (II) is formed.

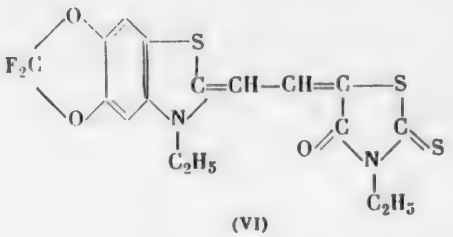
It is interesting to note that the fluorine atoms in the difluoromethylenedioxy group are exceedingly stable toward a number of reactions, for example, heating with sodium hypobromite, phosphorus pentasulfide, etc. As distinct from fluorine, the chlorine atoms in the dichloromethylenedioxy group are readily hydrolyzed by damp air in the cold.

From base (II) was obtained a quaternary salt—the iodoethylate, from which were synthesized five dyes: trimethyncyanine, mesomethyl- and mesoethylthiacarbocyanine, dicarbo- and tricarbocyanines. Absorption maxima from alcoholic solution are given in the table



No. of dye	n	R	λ_{max} in mμ	Displacement of Δ (in mμ)
I	1	H	574	16
II	1	CH_3	556	12
III	1	C_2H_5	561	11
IV	2	H	668	17
V	3	H	776	14

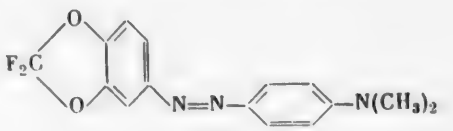
Also synthesized was the merocyanine (VI), λ_{max} 530 mμ, displacement 7 mμ.



(VI)

Thus, introduction of a difluoromethylenedioxy group into the molecule of the thiacyanine dyes causes a displacement of the absorption maximum in the long-wave direction to the extent of 11-17 mμ. The methylenedioxy group shows an even greater effect on color of the dye. Thus, 3,3'-diethyl-5,6,5',6-bis(methylenedioxy)-thiacarbocyanine has absorption maximum 595 mμ [3]. Substitution of hydrogen atoms by fluorine causes a displacement in absorption maximum of the dye in the long-wave direction to the extent of 21 mμ. Hypsochromic displacement of the absorption maximum is observed on substituting a hydrogen atom by a fluorine in the corresponding methoxy- and methylmercapto derivatives also.

On coupling the diazonium salt of 3,4-difluoromethylenedioxyaniline with dimethylaniline, azo dye (A) is obtained.



(A)

In alcohol solution λ_{max} is 420 mμ, ϵ $3.0 \cdot 10^4$; in acid solution [2 volumes of alcohol and 1 volume of hydrochloric acid (d 1.19)] λ_{max} is 524 mμ, ϵ $2.31 \cdot 10^4$.

In its effect on the color of p-dimethylaminoazo dyes the grouping $-O-CF_2-O-$ is similar to weak electropositive substituents (CH_3-, OCF_3-groups).

EXPERIMENTAL

3,4-Difluoromethylenedioxyaniline. Obtained by a Hofmann from 3,4-difluoromethylenedioxybenzamide [2]. A solution of 32.9 g of caustic potash in 256 ml of water was cooled to 0°, 4.7 ml of bromine and 14 g of well-crushed amide added. The mixture was stirred until all the amide went into solution and heated for 20 minutes at 75-80°. Amine was removed by steam distillation. The product was extracted with ether, dried, and distilled. B.p. 95-97° (12 mm). Yield 8.34 g (69.5%).

Found %: N 8.09, 8.10. $C_7H_5O_2NF_2$. Calculated %: N 8.09.

The residue from the steam distillation was acidified with hydrochloric acid. 1.13 g of 3,4-difluoromethylenedioxybenzoic acid was obtained.

3,4-Difluoromethylenedioxybenzoic Acid. 1.94 g of the fluoroanhydride of 3,4-difluoromethylenedioxybenzoic acid was dissolved in acetone and a drop of water added. This was boiled for 1 hour, acetone distilled off, the residue dissolved in 10% soda solution and precipitated with hydrochloric acid. M. p. 153-154° (from aqueous methanol). Yield 1.29 g (67.2%).

Found %: F 18.90, 18.99. $C_8H_4O_4F_2$. Calculated %: F 18.81.

3,4-Difluoromethylenedioxyacetanilide. 7.64 g of 3,4-difluoromethylenedioxyaniline was mixed with 8 ml of acetic anhydride. The mixture became warm and a precipitate separated out. The mixture was diluted with water and sodium acetate added. M.p. 137-138° (from aqueous methanol). Yield 9.12 g (96.1%).

Found %: N 6.82, 6.63. $C_9H_7O_3NF_2$. Calculated %: N 6.51.

3,4-Difluoromethylenedioxythioacetanilide. 6.06 g of 3,4-difluoromethylenedioxyacetanilide was heated with 3.5 g of phosphorus pentasulfide in a test tube, stirring with a rod. Bath temperature was raised to 120°. When the molten mixture became a light-chocolate, the test tube was removed from the bath and stirred. The residue was ground with 2 N caustic soda, and the product precipitated from carbonic acid solution. Yield 4.26 g (65.4%).

2-Methyl-5,6-difluoromethylenedioxybenzthiazole. A cooled solution of 1.2 g of 3,4-difluoromethylenedioxythioacetanilide in 22 ml of 2 N caustic soda was added to 29 ml of a 20% potassium ferricyanide solution cooled to 0°. This was stirred for 1 hour at 0°. The precipitate was filtered off. Steam distillation then took place. M.p. 122-123° (from methanol). Yield 0.6 g (60%).

2-Methyl-5,6-dioxybenzthiazole. 0.1 g of 2-methyl-5,6-difluoromethylenedioxybenzthiazole was heated with 1 ml of 20% hydrochloric acid in a sealed tube at 160-170°. By careful alkalization with sodium bicarbonate, the dioxybenzthiazole was obtained. M.p. 251-252°. Yield 0.03 g.

Found %: N 7.80, 7.77. $C_8H_7O_2NS$. Calculated %: N 7.73.

Iodoethylate of 2-methyl-5,6-difluoromethylenedioxybenzthiazole. 1 g of 2-methyl-5,6-difluoromethylenedioxybenzthiazole was mixed with 0.81 g of diethyl sulfate and heated for 3.5 hours at 100° and for 30 minutes at 115°. The iodide was precipitated by addition of saturated potassium iodide solution. Yield was quantitative.

Dyes

I. 3,3'-Diethyl-5,6,5',6'-bis(difluoromethylenedioxy)thiacarbocyanine Iodide. A mixture of 0.4 g of the iodoethylate of 2-methyl-5,6-difluoromethylenedioxybenzthiazole, 0.4 g of orthoformic ester, 3 ml of pyridine, and 2 drops of acetic anhydride was boiled for 45 minutes. M.p. 277-278° (decomp., from methanol). Yield 0.15 g (44.1%).

Found %: I 19.25, 19.34. $C_{23}H_{17}O_4N_2S_2F_4I$. Calculated %: I 19.48.

II. 3,3'-Diethyl-5,6,5',6'-bis(difluoromethylenedioxy)-9-methylthiacarbocyanine Iodide. Obtained similarly to (I) with orthoacetic ester. M.p. 278-279° (decomp., from methanol). Yield 0.1 g (30%).

Found %: I 18.99, 18.87. $C_{24}H_{19}O_4N_2S_2F_4I$. Calculated %: I 19.07.

III. 3,3'-Diethyl-5,6,5',6'-bis(difluoromethylenedioxy)-9-ethylthiacarbocyanine Iodide. Obtained similarly to (I) with o-propionic ester. M.p. 255-256° (decomp., from ethanol). Yield 0.08 g (18.1%).

Found %: I 18.83, 18.32. $C_{25}H_{21}O_4N_2S_2F_4I$. Calculated %: I 18.66.

IV. 3,3'-Diethyl-5,5'6,6'-bis(difluoromethylenedioxy)thiadicarbocyanine Iodide. A mixture of 0.4 g of the iodoethylate of 2-methyl-5,6-difluoromethylenedioxybenzthiazole, 0.17 g of β-anilinoacroleinanil hydrochloride, and 3 ml of pyridine was boiled for 40 minutes. M.p. 260-261° (from methanol). Yield 0.05 g (14.3 %).

Found %: I 18.71, 17.72. $C_{25}H_{19}O_4N_2S_2F_4I$. Calculated %: I 18.73.

V. 3,3'-Diethyl-5,5',5,6'-bis(difluoromethylenedioxy)thiatricarbocyanine Iodide. A mixture of 0.5 g of the iodoethylate of 2-methyl-5,6-difluorodioxymethylenebenzthiazole, 0.16 g of the hydrochloride of the anilanilide of glutaconaldehyde, 3 ml of anhydrous alcohol, and 3-4 drops of piperidine was boiled for 2 minutes. M.p. 233-234° (decomp.) (from methanol). Yield 0.12 g (26.7%).

Found %: I 18.20, 18.30. $C_{27}H_{21}O_4N_2S_2F_4I$. Calculated %: I 18.04.

VI. 3-Ethyl-5-(3'-ethyl-5',6'-difluoromethylenedioxybenzthiazolinylidene-2-ethylidene)thiazolidinethione-2-one-4. A mixture of 0.38 g of the iodoethylate of 2-methyl-5,6-difluoromethylenedioxybenzthiazole, 5 ml of anhydrous ethanol, and 0.1 g of triethylamine was boiled for 45 minutes. The dye was washed with methanol. M.p. 253-254° (from pyridine). Yield 0.14 g (33.3%).

Found %: N 6.60, 6.64. $C_{17}H_{14}O_3N_2S_3F_2$. Calculated %: N 6.54.

VII. 3,4-Difluoromethylenedioxy-4-dimethylaminoazobenzene. 0.23 g of 3,4-difluoromethylenedioxyaniline was mixed with 0.92 ml of hydrochloric acid (d 1.19) and 3.7 ml of water, cooled to 0°, and diazotized by addition of 0.1 g of sodium nitrate. The diazo solution was neutralized with sodium acetate, filtered, and poured into a solution of 0.18 g of dimethylaniline in 1 ml of 50% acetic acid. The yellow precipitate settling out was filtered off after several hours. M.p. 122-123° (from aqueous methanol), Yield 0.17 g (58.6%).

Found %: N 13.58, 13.56. $C_{15}H_{13}O_2N_3F_2$. Calculated %: N 13.77.

SUMMARY

The synthesis is described of 2-methyl-5,6-difluoromethylenedioxybenzthiazole and six thiacarbocyanine dyes with difluoromethylenedioxy groups as the substituents. It was shown that introduction of a difluoromethylenedioxy group into the molecule of thiacyanine dyes causes a displacement of the absorption maximum in the long-wave direction to the extent of 11-17 mμ.

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All abbreviations of periodicals in the above bibliography are letter-by-letter transliterations of the abbreviations as given in the original Russian journal. *Some or all of this periodical literature may well be available in English translation.* A complete list of the cover-to-cover English translations appears at the back of this issue.

AN INVESTIGATION OF THE REACTION OF FURFUROLE WITH ANILINE

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The formation of resinous products on reacting furfurole with aniline was observed by Stenhouse in 1840 [1]. Preparation of resins from furfurole and various aromatic amines was described by Mains and Phillips [2]. These resins have been suggested for the preparation of varnishes. Beckman and Dehn established that hydrochloric acid has a catalytic effect on the formation of resins from furfurole and amines [3]. In the field of chemical stabilization of priming coats use was found for resins formed in the cold by mixing furfurole and aniline in the molar ratio 1 : 2 [4]. The chemical nature of the resin formation has not been described in the literature. Data occurs on the formation of crystalline condensation products of furfurole and aniline. Chalmot obtained furfuranil – the condensation product of furfurole and aniline – in the molar ratio 1 : 1 [5]. Stenhouse obtained β-hydroxyglutaconaldehydedianil chloride on reacting aniline hydrochloride and furfurole in alcoholic solution [6].

$$[C_6H_5NH{=}CH{-}C(OH){=}CH{-}CH{=}CH{-}NH{-}C_6H_5]^+\,Cl^-$$
Stenhouse's salt

MacGown, reacting Stenhouse's salt with alkali, obtained a crystalline compound corresponding to the condensation product of furfurole with aniline in the ratio 1 : 2 [7]. In the literature, no light has been thrown on the question of the role of these crystalline products in resin formation.

In the study of the chemical nature of resin formation we utilized, besides chemical investigation methods, physicochemical analytical methods. Such a complex approach to the study of the furfurole – aniline system allowed a fuller study of the changes proceeding in it. Properties of the system studied were light-absorption, viscosity, and thermal effect.

In order to follow the formation of the products of the reaction of furfurole and aniline in the first stage of the process, the system aniline – furfurole – hydrochloric acid – acetone was studied. The amount of furfurole and aniline was 20 moles % (HCl 0.0015 mole %). Light-absorption was the property of the system studied. Acetone solutions of furfurole and aniline were prepared immediately prior to the readings. All the chemically pure substances used were first distilled. The corresponding amount of hydrochloric acid was introduced into the aniline solution. After stirring the acetone solutions of furfurole and aniline for 0.5 hours, optical density reached values which remained constant during the readings. On the optical density – composition curves (Fig. 1) a specific point is observed, corresponding to formation of a chemical compound from furfurole and aniline in the molar ratio 1 : 1 in the region 350-360 mμ.

To study the composition of the reaction products of furfurole and aniline at a more advanced stage in resin formation, mixtures of various compositions, obtained by mixing furfurole with aniline and hydrochloric acid in the corresponding molar ratios, were placed in a thermostat at 40° for 7 hours. The resinous product was dissolved in acetone, and measurements of the optical density of the solutions carried out (Fig. 2). Elevation of temperature and increase in hydrochloric acid content promoted resin formation. On the optical density – composition curve (curve 1) several noteworthy points are observed, corresponding to molar ratios of furfurole to aniline equalling 2 : 1, 1 : 1, 1 : 2, 1 : 4, which were reproduced in several experiments and were confirmed on investigating a layer with the amount of furfurole and aniline 40 moles % (HCl 0.012 mole %) (Fig. 2, curve 2). Maintaining the furfurole and aniline mixtures at an elevated temperature leads to fixation of the resin-formation process at a specific stage.

This also explains the recurrence of the results obtained on investigating acetone solutions of furfurole–aniline resins.

In order to ascertain whether these noteworthy points occurring in the optical density–composition diagram would be confirmed on studying other properties of the system, viscosity–composition and thermal effect–composition diagrams were studied. Viscosity of solutions of the system furfurole–aniline–hydrochloric acid–acetone (amount of furfurole and aniline–40 moles %, HCl 0.012 mole %) was measured on an Ostwald viscometer at 35 and 40° in centipoises. In the viscosity–composition diagram of this system the noteworthy point is confirmed (Fig. 3). The abscissa (composition) of this point remains constant with change in temperature (35-40°). Consequently, this noteworthy point is a special point corresponding to the reaction of furfurole with aniline in the molar ratio 1 : 2.

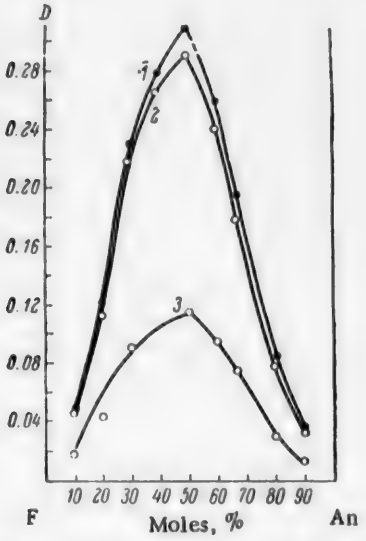


Fig. 1. Optical density (D) of the system aniline (An)–furfurole (F)–hydrochloric acid (HCl)–acetone. Amount of An + + F 20 moles %; HCl 0.0015 mole %, layer thickness 1 mm, (in mμ): 1) 530; 2) 540; 3) 560.

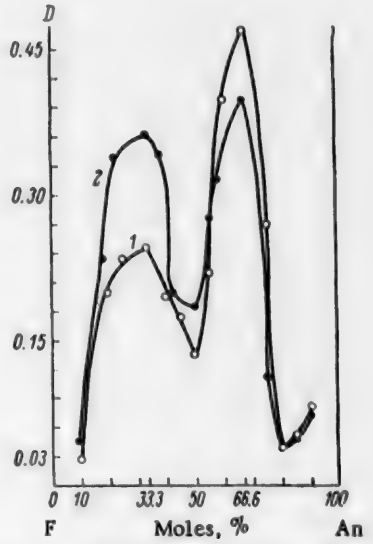


Fig. 2. System furfurole–aniline–hydrochloric acid–acetone (HCl 0.012 mole %). 1) 565 mμ; amount of F and An 20 moles %; 2) 570 mμ; amount of F and An 40 moles %.

In order to study change in viscosity of the furfurole-aniline resins in relation to their composition, the system furfurole-anilinehydrochloric acid was observed. Viscosity was measured on a Heppler viscometer. The mixture of furfurole, aniline, and hydrochloric acid (HCl 0.012 mole %) was placed in the viscometer tube, where it was maintained at the experiment temperature for 0.5 hour. On the viscosity–composition curve at 60° (Fig. 4) a special point is observed as a sharp maximum at molar ratio of furfurole to aniline 1 : 2. System viscosity at this point increases relative to viscosity of initial components more than 1000 times, hence logarithm of viscosity is shown in the diagram. At 70° it was not possible to draw up a viscosity–composition curve owing to thickening of the resin. At 50° the resin had insufficient fluidity. The effect of toluene on position of this special point was also studied. To do this, viscosity of the system furfurole–aniline–toluene–hydrochloric acid was studied (amount of furfurole and aniline 90 moles %, HCl 0.012 mole %). As seen in Fig. 5, toluene addition lowers the viscosity of the system, but does not displace the abscissa (composition) of the special point.

To construct the diagram thermal effect–composition of the system furfurole–aniline–hydrochloric acid was studied (HCl 0.048 mole %). With smaller hydrochloric acid content in the system, resin formation proceeded very slowly, this hampering measurement of thermal effects. In Fig. 6 is shown the thermal effect–composition curve, in which is observed a special point as a maximum corresponding to the reaction of furfurole and aniline in the molar ratio 1 : 2. On formation of the compound corresponding to the special point, 10800 cal. of heat per 1 mole of compound were evolved.

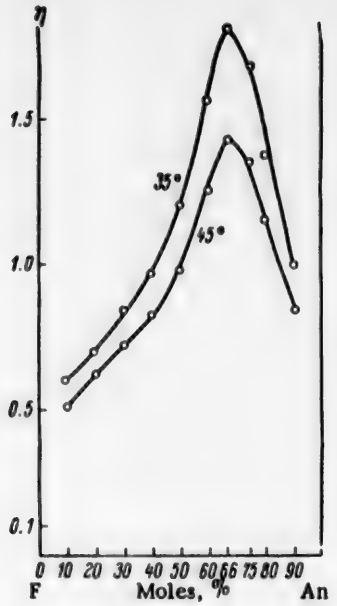


Fig. 3. System furfurole–aniline–hydrochloric acid–acetone. Amount of F and An 40 moles %; HCl 0.012 mole %.

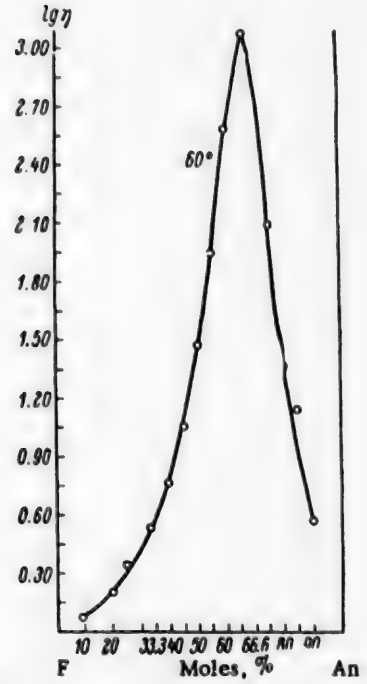


Fig. 4. Logarithm of viscosity of system aniline–furfurole–hydrochloric acid (HCl 0.012 mole %).

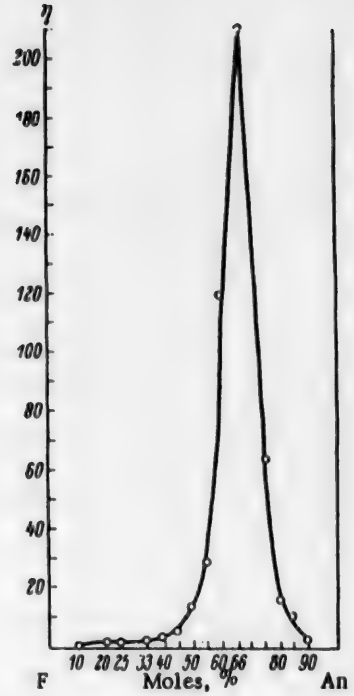


Fig. 5. Viscosity of system aniline–furfurole–hydrochloric acid–toluene. Amount of An + F 90 moles %, HCl 0.012 mole %, toluene 10 moles %.

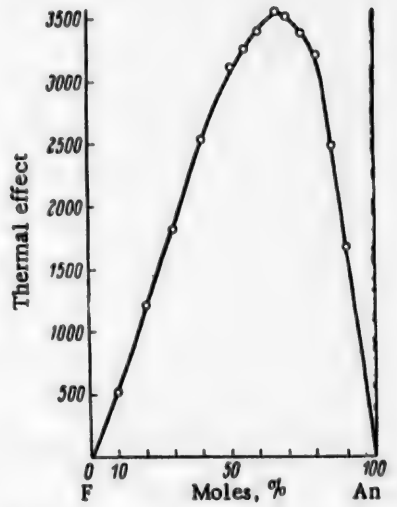


Fig. 6. Thermal effect of system furfurole–aniline–hydrochloric acid (HCl 0.048 mole %).

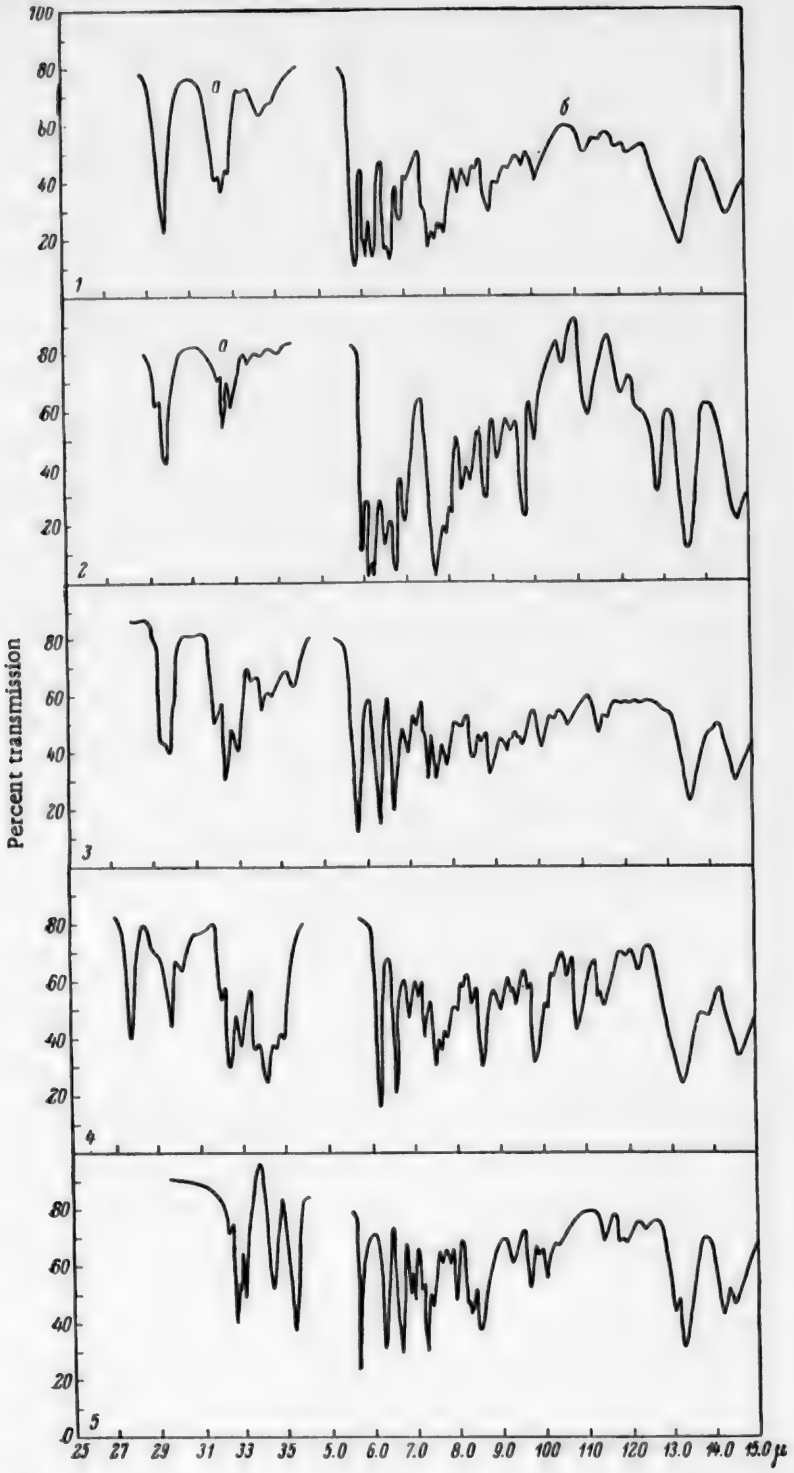


Fig. 7. Infrared spectra. 1) Base of Stenhouse's salt: a LiF prism, CCl_4 solution 0.3%, d 5 mm; b NaCl prism, KBr disk (3 g + 0.005 g); 2) benzylidene derivative (a – CCl_4 solution 0.1%); 3) hydrogenated base (1 mole H_2); 4) hydrogenated base (2 moles H_2); 5) 1,5-diphenylpyrrolidone-3.

TABLE 1. Absorption Frequencies of C = O and C = C Bonds (in cm^{-1})

Prep. No.	Compound	C = O	C = C	Remarks
1	Base of Stenhouse's salt	1712	1639	KBr disks
		1712	1639	Solution in benzene
		1718	–	Solution in pyridine
2	Benzylidene derivative	1689	1639	
3	Hydrogenated base	1735	–	KBr disks
		1742	–	Solution in benzene
		1745	–	Solution in pyridine
4	1,5-Diphenylpyrrolidone-3	1742	–	KBr disks
		1745	–	Solution in benzene
		1755	–	Solution in pyridine

Thus, the special point corresponding to the reaction of furforole aniline in the molar ratio 1 : 2 is confirmed in the constitution–property diagrams on studying a series of properties: light-absorption, viscosity, and thermal effect. The furfurole–aniline resin of composition corresponding to the above special point possesses a greater ability to stabilize priming coats.

The chemical compound corresponding to this point and obtained from the resin appeared identical to the compound obtained by MacGown in solution [7, 8]. At first, MacGowan assigned to the base of Stenhouse's salt the structure 2- or 6-anilino-1-phenyl-1,2,3,6-tetrahydropyridone-3. The position of the double bond was decided by the fact that the u.v. -spectrum of the corresponding toluidine derivative showed slight conjugation [7]. Rombaut and Smets are also inclined to favor these formulas for the base [9], having investigated the u.v. absorption spectra of a series of similar aniline derivatives. MacGown later [8] assigned to the base of Stenhouse's salt the structure 2-anilino-1-phenyl-1,2,3,4-tetrahydropyridone-3, in which conjugation did not occur. This conclusion was based on the fact that the absorption frequency of the carbonyl group in the i.r.-spectrum had the normal value characteristic of unconjugated systems in a six-membered ring. Another possible structure–6-anilino-1-phenyl-1,2,3,4-tetrahydropyridone-3–was rejected by him because the compound studied gave no dibenzylidene derivative.

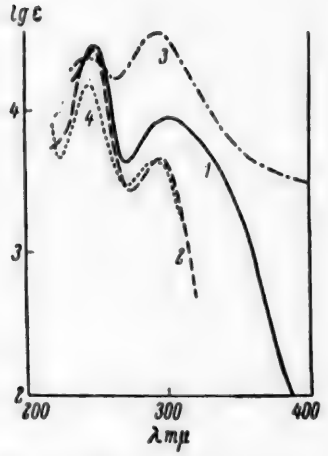


Fig. 8. Ultraviolet spectra in dioxane. 1) Base of Stenhouse's salt; 2) hydrogenated base; 3) benzylidene derivative; 4) 1,5-diphenylpyrrolidone-3.

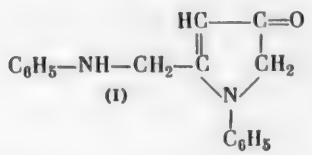
Since the data of the i.r. - and u.v. -spectra conflict with each other (the u.v. -spectrum indicates the presence of conjugation, and the i.r. indicates its absence), MacGowan's synthesis was repeated [7] and the absorption spectra of the base of Stenhouse's salt and its benzylidene derivative investigated (Fig. 7 and 8). Spectral analysis confirmed the above contradiction. To verify the presence of conjugation, quantitative hydrogenation of the double bond was carried out and the spectra of the hydrogenation products obtained (Tables 1, 2; Fig. 7 and 8). In the i.r.-spectrum of the hydrogenated product the double-bond absorption band is absent, and the frequency of the carbonyl group displaced in the direction of higher frequency. This points to the fact that in the intial compound–the base of Stenhouse's salt–the carbonyl group is conjugated with a double bond.

Spectra were taken in dioxane (c $3.75 \cdot 10^{-3}$ m, d 0.1 mm). The presence of conjugation is also confirmed by the u.v. -spectra. The extinction coefficient at λ 295-300 mμ is lowered from 9100 for the base to 4660 for the hydrogenation product. The frequency of the carbonyl group (in the i.r.-spectrum) in the hydrogenated base (where conjugation is absent) has an increased value in comparison with the frequencies in usual conjugated and unstrained systems, i.e., in ketones with an open chain or with a six-membered carbon ring. Displacement of the carbonyl absorption band to the region of higher frequency is observed in the case of strained rings–five- or four-membered [10]. The proposition was therefore put forward that in the initial base a five-membered and not a six-

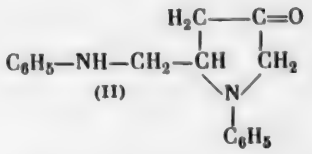
TABLE 2. Maxima and Absorption Coefficients of the C = O Bond in the Ultraviolet Region of the Spectrum

Prep. No.	Compound	λ (in mμ)	ϵ_{max}
1	Base of Stenhouse's salt	300	9100
2	Benzylidene derivative	295	35200
3	Hydrogenated base	295	4660
4	1,5-Diphenylpyrrolidone-3	290	4250

membered ring occurs, and that in the frequency of the C = O bond the influence of two effects is exerted: the effect of conjugation decreasing the frequency, and ring strain increasing it. This also explains why the carbonyl group frequency has a normal value, while the u.v.-spectrum indicates weak conjugation. Thus, for the base of Stenhouse's salt the structure 5-methylanilino-1-phenylpyrrolidone-3 (I) is more likely, and for the hydrogenated base, the formula 5-methylanilino-1-phenylpyrrolidone-3 (II).



(I)



(II)

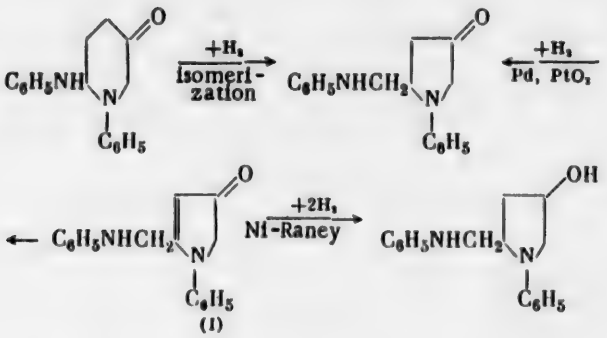
The choice of a formula of structure (I) was made on the basis of spectroscopic data relating to carbon rings. However, in the compounds investigated in a nitrogen heteroatom occurs, which could exert a specific influence on the frequency of the carbonyl group occurring in the β-position. It was impossible to draw a well-defined conclusion from the only three works found in the literature [11-13]. In the first two works, five-membered heterocyclic compounds were investigated containing several different C = O groups, which made interpretation of carbonyl frequencies difficult. In addition, in the work of Davoll [12], carbonyl group frequencies appeared definitely understated and more characteristic of conjugated noncyclic systems. In the work of Leonard and coworkers [13] data is given for the carbonyl frequencies of 1-phenylpiperidone-3 (1722 cm^{-1}) and 1-ethyl-2-phenylpiperidone-3 (1722 cm^{-1}) which are somewhat greater values in comparison with the carbonyl frequency of cyclohexanone (1712 cm^{-1}), which does not point to the possibility of the nitrogen atom having a significant effect on the frequency of the β-carbonyl group in a six-membered heterocycle.

To confirm the proposed formula of structure (I), synthesis of the model compound, 1,5-diphenylpyrrolidone-3*, was carried out and i.r.- and u.v.-spectra taken (Tables 1, 2; Fig. 7, 8). The absorption bands of the carbonyl groups in the hydrogenated base and the model compound are very close. The somewhat lower value of the frequency of the hydrogenated base (KBr discs) can probably be attributed to the intermolecular hydrogen bond. The extinction coefficients of the u.v.-spectra of both compounds appeared close. All this confirms the presence of a five-membered ring in the hydrogenation product.

However, it was impossible not to bear in mind the possibility that the initial base of Stenhouse's salt might contain a six-membered ring which on hydrogenation is converted into a five-membered one as a result of isomerization. To allow for the possible isomerizing action of an arbitarily taken catalyst, hydrogenation was carried out over three different catalysts (Ni-Raney, PtO_2, and Pd on $CaCO_3$). In hydrogenation over platinum and palladium about 1 mole of hydrogen was used and identical products obtained. In hydrogenation over Ni-Raney 2 moles of hydrogen were absorbed. The i.r.-spectrum of the hydrogenation product (Fig. 7) indicated the absence of a carbonyl group

* Synthesis was carried out according to the data in the works of Southwick and coworkers [14, 15].

and of a double bond, and the presence of a hydroxyl absorption band (3571 cm^{-1}). The general hydrogenation scheme, including the possibility of isomerization, can be presented thus.



(I)

Hydrogenation was carried out at atmospheric pressure and room temperature. Considering the mild hydrogenation conditions and also that with two different catalysts the same hydrogenation product was obtained, isomerization on hydrogenation seems rather impossible.

In support of the formulae of structure (I) and (II) can be quoted additional data on their spectra and chemical properties. In the i.r.-spectrum of compound (II) the absorption band 1539 cm^{-1} is absent, this being present in the spectrum of compound (I). Cromwell with coworkers [16] relates this band to the vibration frequencies of the C–N bond of vinylogues of amides (regardless of the degree of hydrogen substitution in the amide group). Formula (I) corresponds to the vinylogue of a disubstituted amide, but in 6-anilino-1-phenyl-1,2,3,4-tetrahydropyridone-3 the vinylogue disappears as a result of hydrogenation. A vinylogue is also observed in the case where compound (I) does not form a semicarbazone or other carbonyl derivatives, whereas (II) was obtained as the semicarbazone of the hydrogenation product.

On the basis of the above, for the base of Stenhouse's salt formula (I) is the most likely, containing a β-pyrrolinone ring. It should be noted that there is little information on β-pyrrolinones in the literature and that they are relatively difficult to prepare. Preparation of a cyclic base by direct reaction of furfurole and aniline appears a simple means of obtaining such compounds.

EXPERIMENTAL*

U.v.-spectra were taken on an SF-4 spectrophotometer; the solvent was dioxane; concentration of solutions was $3.8 \cdot 10^{-3}$ M.

I.r.-spectra were taken on a two-beam recording IKS-2 spectrometer: in the region of the spectrum 2-4 μ a LiF prism was used, in the region of the spectrum 5-15 μ – a NaCl prism. Calibration of the LiF prism was effected with polystyrene, methane, and ammonia, calibration of the NaCl prism – with polystyrene, benzene, and vinylacetylene. Accuracy of wave-length reading was 0.02 μ. In the region of the spectrum of the NaCl prism all substances were taken compressed with KBr. Compression was carried out under a pressure of 10 t/cm^2, using a forvacuum. In the region of the spectrum of the LiF prism spectra were taken in CCl_4 (concentrations shown in Fig. 1).

Base of Stenhouse's Salt (5-Methylanilino-1-phenylpyrrolinone-3) (V). In a porcelain dish were mixed 41.4 ml of furfurole and 91 ml of aniline to which had first been added 0.3 ml of concentrated hydrochloric acid. The mixture was heated on a water bath for 3 hours. The oily product, after cooling to room temperature, solidified and was ground to a light-brown powder. After four-fold recrystallization from benzene (with washing with methanol) pure white, plate-like crystals were obtained with m.p. 144°. Yield 26.5 g (20%).

Found %: C 77.44; H 6.06; N 10.6. M 265 (in benzene). $C_{17}H_{16}ON_2$. Calculated %: C 77.23; H 6.1; N 10.61. M 264.

* The authors express their thanks to I. M. Motkina and B. N. Sverdlova for carrying out the analysis and for participation in the experimental section of the investigation.

Hydrogenation. This was carried out in ethyl acetate at atmospheric pressure and room temperature over three different catalysts: Ni-Raney, Pd on $CaCO_3$, and PtO_2. Hydrogenation was discontinued when rate of hydrogen absorption fell off sharply. This corresponded in the case of Ni-Raney to 2 moles of H_2 to 1 mole of (V) and to approximately to 1 mole of H_2 to 1 mole (V) in the case of $Pd/CaCO_3$ and PtO_2. After completion of hydrogenation, the catalyst was filtered off, and the solvent distilled off in vacuo at room temperature in a steam of H_2. All operations in the isolation of hydrogenation products were carried out immediately after completion of hydrogenation, since on standing the solution rapidly resinified. In the dry condition the hydrogenation products were stable

5-Methylanilino-1-phenyl-3-hydroxypyrrolidine (VIII). For hydrogenation, 1.3 g of (V) in 90 ml of ethyl acetate and about 3 g of Ni-Raney were used. Toward the end of solvent distillation white crystals of (VIII) precipitated, which after two recrystallizations from methanol were dried in vacuo. M.p. 130°. Yield 0.6 g.

Found %: C 76.30; H 7.50. $C_{17}H_{20}ON_2$. Calculated %: C 76.12; H 7.46.

6-Methylanilino-1-phenylpyrrolidone-3 (VI). On hydrogenation of (V) over PtO_2 and Pd on $CaCO_3$, in the hydrogenation products using i.r.-spectra the presence of (V), (VI), and (VIII) was observed, the proportion of which varied somewhat depending on the type of catalyst and its activity; for this reason, the method of preparing (VI) was altered.

5 g of substance (V) in 175 ml of ethyl acetate (0.2 g of PtO_2) was hydrogenated precisely to absorption of 1 mole of H_2 (further of H_2 absorption proceeded very slowly). On distillation of solvent in vacuo the first fraction of the crystals precipitating (2 g) was separated, and the mother liquor further concentrated in vacuo. To the viscous product was added a small amount of methanol, and after sometime crystals precipitated (1.6 g). The first fraction of the crystals contained (VI) with excess (V)(according to the data of the i.r.-spectrum). The second fraction was recrystallized twice from CCl_4; white crystals were obtained with m.p. 114.5-115°.

Found %: C 76.7; H 6.73; N 10.85. M 265 (in benzene). $C_{17}H_{18}ON_2$. Calculated %: C 76.7; H 6.77; N 10.51, M 266.

Semicarbazone: m.p. 120-125° (decomp.).

Found %: N 20.7. $C_{18}H_{21}ON_5$. Calculated %: N 21.6.

SUMMARY

1. To study the formation of a furfurole-aniline resin, physicochemical methods as well as chemical methods were used. Properties of the system studied were light-absorption, viscosity, and thermal effect. In the composition–property diagrams, noteworthy points were observed, corresponding to molar ratios of furfurole and aniline of 2 : 1, 1 : 1, 1 : 2, 1 : 4.

2. The noteworthy point 1 : 2 was confirmed for a series of properties and proved to be a special point corresponding to formation of a chemical compound. A compound of such composition was isolated from the resin in crystalline form and its hydrogenation products obtained. On the basis of the study of i.r.- and u.v.-spectra of the compounds indicated, and also of a model compound–1,5-diphenylpyrrolidone-3–for the product isolated from the resin (the base of Stenhouse's salt) was proposed a formula of structure corresponding to 5-methylanilino-1-phenylpyrrolidone-3.

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ISOTOPIC EXCHANGE IN DECARBOXYLATION OF DEUTERATED BENZOIC ACID

G. A. Semenov, M. Ya. Turkina, and B. V. Shiryaev

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Original article submitted March 15, 1960

While studying the decarboxylation conditions for benzoic acid deuterated in the ring in a quinoline medium, we encountered the occurrence of isotopic deuterium dilution. In the present work are communicated the results of the first stage of the investigations devoted to clarification of the mechanism of the isotopic exchange reaction.

Deuterated benzoic acids were prepared by oxidizing the corresponding deuterated toluenes by boiling with potassium permanganate [1]. The benzoic acid obtained was recrystallized from water, dried at 80-100°, and purified additionally by sublimation in vacuo. The isotopic constitution of the hydrogen in the benzoic acid ring of the benzoic acid was determined by low-voltage mass-spectrometry [2]. The MI-1301 mass-spectrometer worked on a ionizing voltage of 16 V. The ionized benzoic acid vapors gave a molecular ion spectrum corresponding to the separate isotopic forms. The mass-spectrometer was equipped with a mass number indicator based on the measurement of the Hall effect in germanium. Accuracy of mass number measurement fell within ±0.4 mass units. Decarboxylation of benzoic acids was effected by boiling a solution of the acid in quinoline in the presence of powdered cupric oxide [3] for 6-7 hours. Benzene formed was collected in a receiver cooled with solid carbon dioxide, in it the isotopic composition of the hydrogen also being determined by low-voltage mass-spectrometry [2].

In the present work was studied the decarboxylation of the benzoic acids obtained by oxidizing o- and p-deuterotoluenes and toluene strongly enriched with deuterium in the benzene ring [sample 1, 2, and 3]. During decarboxylation of the benzoic acid from p-deuterotoluene (sample 2) two benzene fractions were selected—1.5 and 5 hours after the onset of decarboxylation (see Table 1).

It is noted that in all cases observed, a decrease occurred in deuterium content of the benzene compared with that of the benzene ring of deuterated benzoic acid. Possible reasons for this effect could be isotopic exchange: 1) of the benzoic acid, 2) of a possible intermediate product—copper benzoate, or 3) of benzene with the quinoline.

To investigate the possibility of isotopic exchange between initial benzoic acid and quinoline, a solution of the acid deuterated in the ring with a known degree of isotopic enrichment was boiled for 5 hours with quinoline. Under these conditions marked decarboxylation of benzoic acid was not observed. Isotopic constitution of the acid before and after boiling with quinoline was determined on the mass-spectrometer (Table 2).

It is evident that no appreciable substitution of deuterium in the benzoic acid ring by hydrogen occurs.

Although it is known that deuterium exchange when bonded with carbon in the absence of a specific catalyst is very difficult [4], experiments were conducted to confirm the absence of deuterium exchange in the different isotopic forms of benzene both with quinoline and between themselves. The possibility of the latter exchange in the presence of aluminum chloride had already been indicated in earlier works [5]. During the boiling of deuterium-enriched benzene with quinoline in the presence of cupric oxide two benzene fractions were withdrawn 1.5 and 5 hours after initiation of boiling.

The results of mass-spectrometrical analysis of benzene before and after boiling (Table 3) indicate the absence of isotopic dilution of the deuterated benzene.

The experiments conducted show that in the absence of cupric oxide no isotopic exchange is observed either directly between benzoic acid molecules or between benzoic acid and quinoline. The final decarboxylation product—benzene—also is incapable of isotopic exchange with the quinoline, even in the presence of cupric oxide; thus it can be considered definite that the isotopic exchange reaction is an associated catalytic decarboxylation reaction. There still remains the problem of determining whether the decarboxylation process is the actual cause of the iso-

TABLE 1.

Sample No.	Benzoic acid: Mass	Benzoic acid: content (in %)	Benzoic acid: D content (in at. %)*	Benzene: Mass	Benzene: content (in %)	Benzene: D content (in at. %)
1	123	45.9±0.5	9.4	79	38.1±0.5	7.6
	122	54.1±0.5		78	61.9±0.5	
2	123	31.3±0.1	6.3	79	28.5±0.3	5.6 1st fraction
	122	68.7±0.1		78	71.5±0.3	
				79	26.6±0.3	5.3 2nd fraction
				78	73.4±0.3	
3	127	61.2±0.2	89.7	83	44.5±0.2	85.1
	126	30.8±0.1		82	38.3±0.1	
	125	6.5±0.1		81	13.60±0.05	
	122	1.40±0.07		80	2.50±0.05	
				78	0.90±0.01	

* In calculating deuterium content in at. %, attention was given only to the 5 D atoms of the benzene ring.

TABLE 2.

Mass	Benzoic acid: before boiling with quinoline: content (in %)	Benzoic acid: before boiling with quinoline: D content (in at. %)	Benzoic acid: after boiling with quinoline: content (in %)	Benzoic acid: after boiling with quinoline: D content (in at. %)
127	15.5±0.3		15.3±0.1	
126	60.8±0.3		60.7±0.1	
125	20.6±0.1		20.9±0.1	
124	3.1±0.1	77.7	3.1±0.1	77.6

TABLE 3.

Mass	Benzene before boiling: content (in %)	Benzene before boiling: D content (in at. %)	Benzene after boiling: 1st fraction: content (in %)	Benzene after boiling: 1st fraction: D content (in at. %)	Benzene after boiling: 2nd fraction: content (in %)	Benzene after boiling: 2nd fraction: D content (in at. %)
84	34.6±0.6		35.5±0.3		35.0±0.6	
83	15.4±0.3		15.1±0.2		15.0±0.6	
82	2.8±0.1	49.4	2.9±0.1	50.0	2.8±0.2	49.4
78	47.4±0.9		46.6±0.1		47.1±0.5	

topic exchange reaction or whether isotopic exchange, catalytically accelerated by cupric oxide, can take place under conditions where decarboxylation does not occur.

In conclusion, the authors express their sincere gratitude to A. I. Brodskii and I. P. Gragerov for their discussion of the present work.

SUMMARY

1. Isotopic exchange of the hydrogen of benzoic acid deuterated in the ring was observed on decarboxylating it in a quinoline solution.

2. Experimental proof was given of the absence of isotopic hydrogen exchange in the initial and final decarboxylation products (benzoic acid and benzene).

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A STUDY OF THE COMPOUNDS CONSTITUTING THE ETHEREAL OILS

I. ISOMERIZATION OF CEDRENE OXIDE

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Institute of Chemical Sciences, Academy of Sciences, Kazakh, SSR
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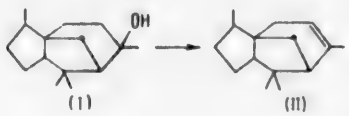
In the territory of Kazakhstan and Central Asia considerable areas are occupied by juniper woods. With proper organization of the extraction of ethereal juniper oils, one of the components—the tricyclic sesquiterpene alcohol cedrol (I) [1]—could become available as a product. It is known that after a series of pharmacological trials the cedrol fractions of juniper oils were recommended as an effective antiseptic [2]. Thus, a study of the chemistry of cedrol is of interest from the point of view of the possibility of preparing on its basis a series of substances with potential physiological activity.

Treibs, treating cedrene glycol (III) with hot 30% sulfuric acid, isolated a liquid product to which he assigned the structure of the α-oxide of cedrene (IV) [8]. Naves et al., oxidizing cedrene with hydrogen peroxide in an acetic anhydride medium, obtained a saturated ketone, $C_{15}H_{24}O$, named by them cedranone (V) [4]. The constants of the cedrene "oxide" of Treibs and the cedranone of Naves are rather close to each other. This gave Naves a basis for proposing that Treibs had not obtained an oxide of cedrene, but cedranone.

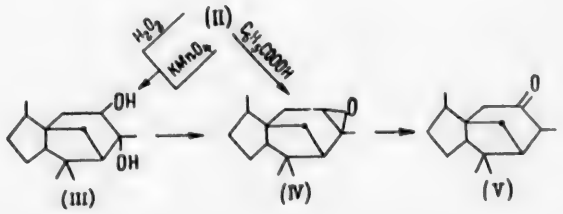
In the present work a study is made of the isomerization of the α-oxide of cedrene (II), which is readily obtained by dehydrating cedrol.



(I) (II)

The cedrene oxide was prepared by oxidizing cedrene with perbenzoic acid with a yield of about 85%. On isomerizing the oxide with sulfuric acid, a ketone $C_{15}H_{24}O$ was obtained in good yield, its constants being close to the constants of the cedranone of Naves and the "oxide" of Treibs (Table).

The ketone has in its infrared spectrum a band with frequency 1700 cm^{-1}, characteristic of the carbonyl group in a six-membered ring. The ultraviolet spectrum of a heptane solution of the 2,4-dinitrophenylhydrazone of cedranone has a maximum at 346 mμ. According to an empirical rule introduced by Nazarov and coworkers [5], such a maximum value is characteristic of ketones containing no double bond linked with a carbonyl. Oxidation of cedrene, according to Naves, led to a product identical with the ketone obtained from the α-oxide of cedrene. There is no doubt that Treibs also obtained cedranone. Thus, all the known conversions of cedrene can be represented by the following scheme.



Constants	"Oxide" of Treibs	Cedranone of Naves	Ketone from α-oxide
B. p.	148 (20 mm)	134 (4 mm)	110—111 (1 mm)
d_4^{20}	1.0062	1.0024	0.9992
n_D^{20}	1.4985	1.4998	1.4986
$[\alpha]_D^{20}$	—	—84.7°	—87.5°

Cedrene oxide isomerizes very readily. Thus, on standing a solution of the oxide in chloroform for a month, spontaneous isomerization proceeded, evoked, evidently, by atmospheric carbon dioxide. The infrared spectrum of the purest of the cedrene oxide samples isolated has a weak absorption band—about 1700 cm^{-1}, indicating a slight trace of cedranone.

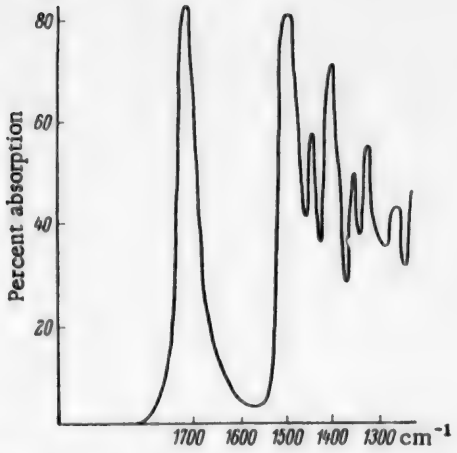
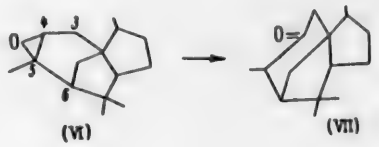


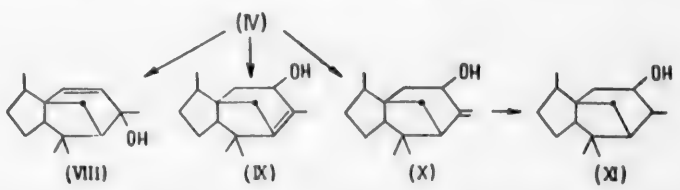
Fig. 1. I.r.-spectrum of isocedranone (prism of NaCl, l 0.01 mm).

The ready isomerizability of cedrene oxide can be explained by the tendency of the strained structure (VI), where carbon atoms 3, 4, 5, and 6 must be coplanar, to go over to the conformationally more favorable structure (VII) with the cyclohexanone ring in the form of a chair.



(VI) (VII)

On isomerizing cedrene oxide with zinc bromide, as the main reaction product cedranone was obtained and a small amount of a crystalline substance with m.p. 129.4-129.8°, hydrogenated on platinum by the method of Adams with absorption of 1 mole of hydrogen into the saturated alcohol $C_{15}H_{24}O$ (XI) with m.p. 143.5-144°, which on oxidation with chromic acid was converted into cedranone, identified by the semicarbazone. The unsaturation of the crystalline alcohol obtained from cedrene oxide was also demonstrated by oxidation with perbenzoic acid into the α-oxide with m.p. 108.3-108.6°. In the literature, cases are described of conversion of oxides into isomeric allyl alcohols [6]. If the isomerization of cedrene oxide is considered in this connection, then it should proceed in the following possible varying ways.



Structure (VIII) was rejected on the grounds that on oxidizing the saturated alcohol $C_{15}H_{26}O$ (XI) with m.p. 143.5-144° cedranone was obtained. Structure (IX) is rather improbable in view of Bredt prohibition. The presence in the infrared spectrum of the unsaturated alcohol of the frequencies 1640, 903, and 3098 cm^{-1} indicates that the double bond is semicyclic [8]. Thus, to the unsaturated alcohol obtained by isomerizing cedrene oxide can be ascribed the structure (X), and for it is proposed the name isocedrenol. It seems expedient to call the ketone obtained previously by Treibs and Naves, and isolated by us, not cedranone, but isocedranone. The necessity of this becomes evident when it is noted that the ketone $C_{15}H_{22}O$ (XII), obtained by oxidizing cedrene with chromic anhydride, is called cedrenone in the literature [7, 9, 10]. Its conversion products—the saturated ketone (XIII) and the unsaturated alcohol (XIV) are correspondingly named cedranone and cedrenol [9].

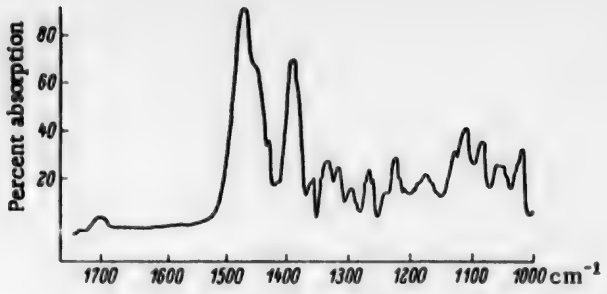


Fig. 2. I.r.-spectrum of the α-oxide of cedrene (prism of NaCl, *l* 0.005 mm).

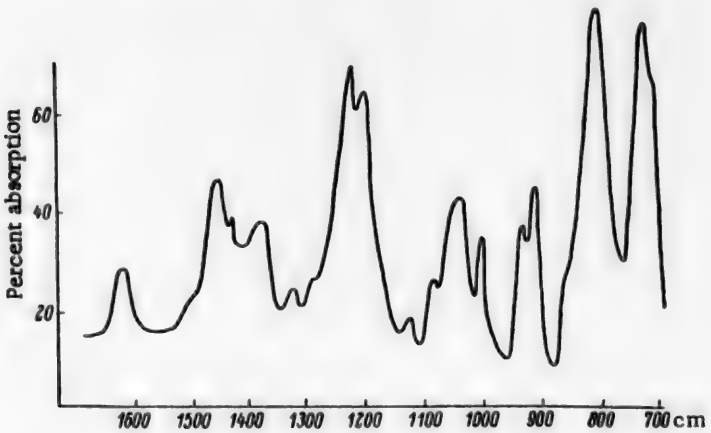


Fig. 3. I.r.-spectrum of isocedrenol (prism of NaCl, solvent CCl_4, *l* 0.1 mm).

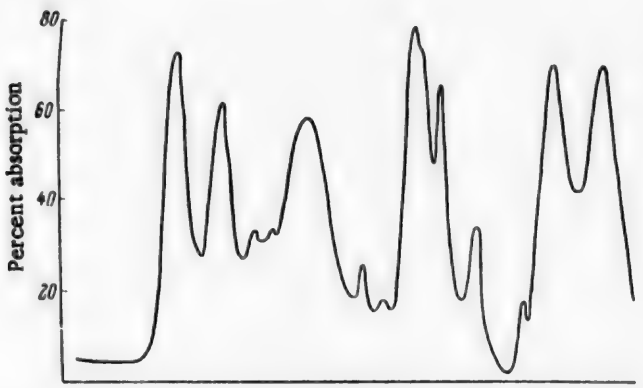
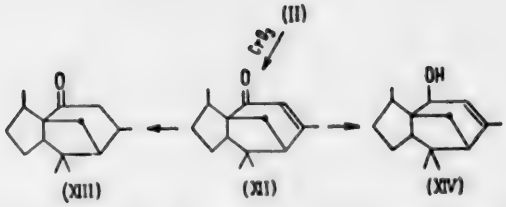


Fig. 4. I.r.-spectrum of isocedranol (prism of NaCl, solvent CCl_4, *l* 0.1 mm).



It should be noted that the very fact of the formation of an unsaturated alcohol confirmed for the initial product the structure of the α-oxide of cedrene, since when isomerized by acidic agents isocedranone is not isomerized into isocedranol.

To decide the position of the double bond in isocedrenol, it was oxidized with chromic anhydride. However, instead of the expected α, β-unsaturated ketone (XV), isocedranone was obtained as the semicarbazone. Thus, in an acidic medium isomerization of isocedrenol into isocedranone occurs, this being in agreement with conversions of allyl alcohols into isomeric carbonyl compounds described in the literature [6]. An experiment in isomerizing isocedrenol in benzene solution by reaction with sulfuric acid also led to the formation of isocedranone.

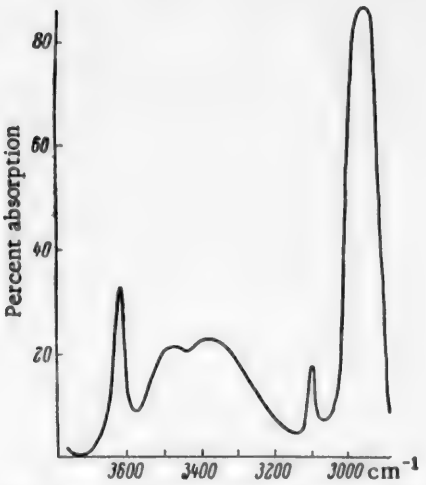
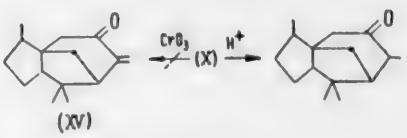
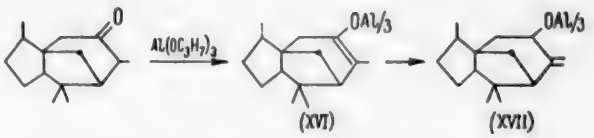


Fig. 5. I.r.-spectrum of isocedrenol (prism of LiF, solvent CCl_4, $\underline{l}$ 0.3 mm).



Isocedranone is characterized by low reactivity. Thus, its semicarbazone can be obtained only after prolonged standing of the reagent mixture in alcoholic-aqueous solution, although Naves [4] noted that it does not form a semicarbazone.

Hydrogenation of isocedranone on a nickel frame was not possible, and reduction with aluminum isopropylate led to completely unexpected results. Instead of isocedranol (XI), obtained by hydrogenating isocedrenol or its stereoisomer, isocedrenol (X) was obtained with a yield of about 60%. This case of an anomalous course for a Meerwein-Ponndorf reaction can be explained by the enolizing action of aluminum isopropylate. Evidently, the conformationally unfavorable structure of the enol (XVI) is regrouped into the more stable isocedrenol alcoholate (XVII).



To confirm this reaction scheme, isomerization of isocedranone by the action of sodium isoamylate was carried out. In this case, isocedrenol was obtained with a yield of about 25%. The latter case evidently confirms the course of the isomerization of ketone (V) into unsaturated alcohol (X) via enol form (XVI).

EXPERIMENTAL

Cedrol was isolated from the ethereal oil of the hemispherical juniper (Juniperus semiglobosa Rgl.) and had m.p. 85-85.5° (from aqueous methanol).

Cedrene was obtained by dehydrating cedrol with 99% formic acid, and exhibited the unusually high optical activity of $[\alpha]_D^{20}$ -96.5°. The extremely high angle of rotation of cedrene of $[\alpha]_D^{20}$ -91.7° was described by Naves [4].

1. Cedrene Oxide. 15.5 g (0.075 mole) of cedrene (n_D^{20} 1.4977, d_4^{20} 0.9316) oxidized with 0.08 mole of perbenzoic acid dissolved in 250 ml of chloroform. The reaction proceeded gently, and for its completion the mixture was allowed to stand for 24 hours at 0° and for the following 24 hours—at room temperature. The solution was washed with 10% caustic soda solution, then with water, and dried with magnesium sulfate. After solvent removal, the product was distilled in vacuo. 13.9 g (84.3%) of oxide was obtained as a colorless liquid. Yield in the individual experiments varied between 80 and 90%.

B. p. 120-120.5 (5 mm), n_D^{20} 1.4967, d_4^{20} 1.0032, $[\alpha]_D^{20}$ -91.4°, MR_D 64.25; calc. 64.31.

Found %: C 81.67; H 10.90. $C_{15}H_{24}O$. Calculated %: C 81.77; H 10.97.

2. Isomerization of Cedrene Oxide with Sulfuric Acid. 4.40 g (0.02 mole) of cedrene oxide was dissolved in 20 ml of dry benzene and after addition of a pumice fragment moistened with 50% sulfuric acid, the solution was boiled for 30 minutes. The reaction mixture was washed with soda solution, then with water, and dried with calcined magnesium sulfate. After elimination of benzene, the product was dissolved in 10 ml of petroleum ether and chromatographed on 200 g of neutral aluminum oxide (activity III—IV). 4.10 g of isocedranone was washed out with petroleum ether.

B. p. 110-111° (1 mm), n_D^{20} 1.4986, d_4^{20} 0.9992, $[\alpha]_D^{20}$ -87.5°, MR_D 64.71; calc. 64.88.

Found %: C 82.04; H 10.90. $C_{15}H_{24}O$. Calculated %: C 81.77; H 10.97.

Semicarbazone. Obtained in almost quantitative yield after allowing to stand for a month a mixture of 1.5 g of ketone, 1.5 g of semicarbazide hydrochloride, and 1.0 g of anhydrous sodium acetate in 15 ml of 80% alcohol. M.p. 185-186° (decomp., from 60% alcohol).

Found %: N 14.92. $C_{16}H_{27}ON$. Calculated %: N 15.14.

2,4-Dinitrophenylhydrazone. Obtained both from the oxide and from isocedranone by the method of Johnson [11]. Very difficult to purify. M.p. 202-204° after repeated chromatography on aluminum oxide and recrystallization from alcohol.

Found %: N 13.83. $C_{21}H_{28}O_4N_2$. Calculated %: N 13.99.

3. Isomerization of Cedrene Oxide with Zinc Bromide. 4.40 g (0.02 mole) of cedrene oxide was dissolved in 20 ml of dry benzene and after addition of 0.05 g of freshly melted zinc bromide the mixture was boiled for 20 minutes. After elimination of benzene, the product was dissolved in 10 ml of petroleum ether and chromatographed on 200 g of neutral aluminum oxide (activity III-IV). 3.50 g of isocedranone with n_D^{20} 1.4985 was washed out with petroleum ether. On elution with alcohol, 0.57 g of isocedrenol was obtained, which after three recrystallizations from petroleum ether melted at 129.4-129.8°. Long needles, subliming even at room temperature.

Found %: C 81.93; H 10.95; OH 1.005 (by the Chugaev-Tserevitinov method). $C_{15}H_{24}O$. Calculated %: C 81.77; H 10.97; OH 1.

Phenylurethane of isocedrenol—a viscous, noncrystallizing liquid.

Naphthylurethane. Obtained by boiling for 2 hours equivalent amounts of isocedrenol and naphthylisocyanate in petroleum ether solution (80-90°). After repeated recrystallization from a mixture of petroleum ether and acetone, m.p. was 130-131°.

Found %: N 3.63. $C_{26}H_{31}O_2N$. Calculated %: N 3.59.

4. Hydrogenation of Isocedrenol. 0.2204 g (0.001 mole) of isocedrenol was hydrogenated in solution in 10 ml of glacial acetic acid on 0.022 g of PtO_2 (prepared by the method of Adams) and discontinued after absorption of 25.5 ml of hydrogen (98%). The mixture was washed with 50 ml of water, neutralized with soda, and extracted with ether. 0.2056 g (92%) of isocedranol was isolated with m.p. 143.5-144° (from petroleum ether). A sample mixed with isocedrenol melted over the range 124-131°. In the infrared spectrum of isocedranol, absorption bands at about 903 and 1640 cm^{-1}.

5. Oxidation of Isocedranol. 0.44 g (0.002 mole) of isocedranol was dissolved in 5 ml of glacial acetic acid, then a solution of 0.5 g of chromic anhydride in 5 ml of glacial acetic acid and 0.5 ml of water added. The mixture was allowed to stand for 48 hours at room temperature. The green solution was poured into 50 ml of water,

neutralized with soda, and extracted with ether. After removal of ether, the residue was chromatographed on 25 g of neutral aluminum oxide (activity III-IV). 0.21 g of isocedranone was washed with petroleum ether, and was identified as the semicarbazone with m.p. 184-186°, giving no depression with the semicarbazone of the isocedranone obtained by isomerizing cedrene oxide.

6. Oxidation of Cedrene [4]. 5 g of cedrene was dissolved in 5 ml of acetic anhydride, to which had first been added 0.25 ml of sulfuric acid (d 1.98). 3 ml of 30% hydrogen peroxide was added to the mixture with stirring and heating (temperature of bath 35-45°) every half hour in 0.5 ml lots. After standing overnight, the mixture was heated for 1 hour on a boiling water bath and poured into 50 ml of water. The solution was neutralized with soda and extracted with ether. After extraction, about 1.5 g of brown substance insoluble in ether remained. After removal of ether the substance was distilled, and the product chromatographed on 100 g of neutral aluminum oxide (activity II-III). 3.15 g (58.5%) of isocedranone was washed out with petroleum ether.

B.p. 110-112° (1 mm), n_D^{20} 1.4985, d_4^{20} 0.9945, α_D^{20} +82.3°, MR_D 64.73; calc. 64.88.

Semicarbazone, obtained by the method described above, melted at 184.5-186°, and gave no melting point depression when a sample was mixed with the semicarbazone of the isocedrenone obtained by isomerizing cedrene oxide.

7. α-Oxide of Isocedrenol. 1.10 g (0.005 mole) of isocedrenol was oxidized in solution in 25 ml of chloroform with perbenzoic acid containing 0.007 M of active oxygen. After standing for 24 hours at 0°, the solution was shaken with 5 g of calcium hydroxide to free it of benzoic acid. The residue was drawn off and washed with dry chloroform. The solvent was distilled off in vacuo, and the residue recrystallized from petroleum ether. After five recrystallizations, 0.72 g (60%) of the α-oxide of isocedrenol was obtained as long needles with m.p. 108.3-108.8°. By allowing the ethereal solution to evaporate slowly it was possible to obtain crystals of the oxide as prisms 3-4 cm long.

Found %: C 76.10; H 10.22. $C_{15}H_{24}O_2$. Calculated %: C 76.38; H 10.25.

8. Hydrogenation of Isocedranone. 2.20 g (0.01 mole) of isocedranone was hydrogenated in solution in 20 ml of alcohol on a nickel frame prepared from 3 g of 33% Ni/Al alloy. Hydrogen absorption was not observed even at a temperature of 40°. After removal of solvent, unchanged isocedranone was obtained.

9. Isomerization of Isocedranone. 2.20 g (0.01 mole) of isocedranone was boiled in solution in 20 ml of benzene with 0.05 g of zinc bromide for 2 hours. After removal of solvent, unchanged isocedranone was obtained.

10. Oxidation of Isocedrenol. 0.44 g of isocedrenol was dissolved in 5 ml of glacial acetic acid, then a solution of 0.50 g of chromic anhydride in 5 ml of acetic acid and 0.5 ml of water added. The mixture was allowed to stand for 48 hours at room temperature. The solution was poured into 50 ml of water, neutralized with soda and extracted with ether. After drying the ethereal solution and removal of solvent, the product was chromatographed on 20 g of neutral aluminum oxide (activity III-IV). 0.12 g of a colorless liquid with n_D^{20} 1.4990 was washed out with petroleum ether.

Semicarbazone had m.p. 184-186° and gave no melting point depression when a sample was mixed with the semicarbazone of the isocedranone obtained by isomerizing cedrene oxide.

11. Isomerization of Isocedrenol. 0.44 g (0.002 mole) was dissolved in 10 ml of benzene, and after addition of a pumice fragment moistened with 50% sulfuric acid, the solution was boiled under a reflux condenser for 5 hours. The mixture was washed with soda solution, then with water, and after removal of part of the benzene, was chromatographed on 20 g of neutral aluminum oxide (activity III). 0.21 g of isocedranone was washed out with petroleum ether.

Semicarbazone melted at 185-186.5°.

12. Isomerization of Isocedranone. 4.40 g (0.02 mole) of isocedranone was added to 30 ml of 1 M aluminum isopropylate solution in isopropyl alcohol. The mixture was placed in a flask fitted with a herringbone dephlegmator, and heated so that 2-5 drops of distillate came over per minute. According to the rate of distillation, dry isopropyl alcohol was added to the flask to maintain constant volume. With 2,4-dinitrophenylhydrazine, liberation of acetone from a sample was not observed. To the mixture was added a further 30 ml of 1 M aluminum isopropylate solution, isopropyl alcohol evaporated off, and after adding 25 ml of dry toluene the contents of the flask were boiled under a reflux condenser for 4 hours. Then 25 ml of dry isopropyl alcohol was added to the reaction mixture and distillation

begun at the rate of 1-2 drops per minute. Evolution of acetone was not observed, although distillation lasted 8 hours. The toluene solution was poured into 50 ml of water and strongly acidified with 10% sulfuric acid. The upper layer was separated off, washed with 5% ammonia solution, then with water. The lower layer was extracted with ether. After drying the united extracts with sodium sulfate, the solvent was distilled off in vacuo. 3.10 g of crude isocedrenol was obtained. After two recrystallizations from petroleum ether, the product melted at 129.2-129.5°. A sample mixed with the isocedrenol obtained by isomerizing cedrene oxide gave no melting point depression. The residue was chromatographed on 25 g of neutral aluminum oxide (activity II-III). 1.10 g of isocedranone was washed out with petroleum ether.

In the following experiments, isomerization was carried out by boiling in a toluene solution equimolecular amounts of isocedranone and aluminum isopropylate.

13. Isomerization of Isocedranone. 1.65 g (0.0075 mole) of isocedranone was added to 20 ml of anhydrous isoamyl alcohol in which had first been dissolved 0.70 g of metallic sodium. The mixture was boiled under a reflux condenser for 5 hours. The solution was poured into 50 ml of water and made acid to Congo with sulfuric acid. The isoamyl alcohol was distilled off in vacuo as an azeotropic mixture with water. The residue was extracted with ether. After drying the ethereal solution and removal of solvent, the product was chromatographed on 80 g of neutral aluminum oxide (activity II-III). 0.81 g of isocedranone was washed out with petroleum ether, and 0.39 g of isocedrenol with m.p. 129.3-129.6° (from petroleum ether) washed out with alcohol. It did not give a melting point depression with the isocedrenol obtained in the previous experiment.

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SUMMARY

1. Cedrene oxide was obtained by oxidizing cedrene with perbenzoic acid.
2. Isocedranone was obtained by isomerizing cedrene oxide with sulfuric acid.
3. Isocedrenol, along with isocedranone, was obtained by isomerizing cedrene oxide with zinc bromide.
4. Isocedranol was obtained by hydrogenating isocedrenol. The oxide was obtained by oxidizing isocedrenol.
5. Conditions for mutual conversion between isocedranone and isocedrenol were determined.
6. Several more rational names were suggested for a series of cedrane derivatives.

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THE REACTION OF OXIDES OF HIGHER UNSATURATED ACIDS WITH LITHIUM ALUMINUM HYDRIDE

I. EPOXYOLEIC ACID AND EPOXYPETROSELINIC ACID

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This investigation continues the series devoted to study of the properties of oxides of higher unsaturated acids [1, 2].

In the present work we found that reduction of the epoxyacids by lithium aluminum hydride gives the corresponding diols. Reduction, for example, of the oxide of oleic acid (cis-Δ^9-octadecenoic acid) gave octadecane-1,10-diol; reduction of the oxide of petroselinic acid (cis-Δ^6-octadecenoic acid) gave octadecane-1,7-diol. Opening of the oxide ring accordingly proceeds preferentially in one direction. We observed a similar phenomenon earlier in the catalytic hydrogenation of oxides of unsaturated acids [2] and in their reaction with ammonia [1].

The purity of the diols that we obtained was confirmed by chromatography. The position of the secondary hydroxyl group was confirmed by comparison of the properties of the ketooctadecanoic acids (obtained by oxidation of the octadecanediols) with those of specially synthesized 10-keto- and 7-keto-octadecanoic acids. The latter were obtained by organocadmium synthesis as employed for preparation of 10-keto-13-methyloctadecanoic acid [3].

EXPERIMENTAL

Preparation of epoxyoleic acid. Saponification of 30 g of triolein trioxide (m.p. 57-58°) [4] was effected with 0.5 N alcoholic potassium hydroxide. After recrystallization from alcohol, the oxide had m.p. 54° [5]. Yield 93%.

Reduction of epoxyoleic acid. To an ethereal solution of the epoxy acid (18 g) was added 35 ml of ethereal solution of lithium aluminum hydride (3.4 g $LiAlH_4$). After completion of the addition, the reaction mixture was heated for 4 hr. The product was recrystallized from alcohol and then from ligroine. M.p. 69-69.5°. Yield 80%.

Found %: C 75.75, 75.77; H 13.39, 13.49. Acid number 0. Number of OH groups 1.95, 1.93. $C_{18}H_{38}O_2$. Calculated %: C 75.46; H 13.37. Acid number 0. Number of OH groups 2.

Part of the octadecane diol (1.2 g) was chromatographed in a column filled with neutral aluminum oxide (100 g, 3rd activity). The compound was eluted with a mixture of ligroine and ethyl ether (1 : 5). Three fractions were collected: 1st 0.7 g, m.p. 69.5°; 2nd 0.3 g, m.p. 69.5°; 3rd 0.06 g, m.p. 69°. No melting point depressions in mixed tests of each of the fractions with the adjacent fractions.

Oxidation of the diol. The octadecanediol (3 g) was oxidized with chromic acid (2.1 g) and glacial acetic acid at room temperature. The product of oxidation, purified by recrystallization from alcohol, had m.p. 78-78.5° [6]. Yield 95%.

Found %: C 72.49, 72.31; H 11.63, 11.64. Acid number 190, 189.5. Number of OH groups 0.99, 1.02. $C_{18}H_{34}O_3$. Calculated %: C 72.43; H 11.48. Acid number 188. Number of OH groups 1.

The semicarbazone of ketooctadecanoic acid had m.p. 101-102° [7].

Found %: N 12.01, 11.95. $C_{19}H_{37}O_3N_3$. Calculated %: N 11.82.

Preparation of octyl bromide. A mixture of octyl alcohol (30 ml) and 40% hydrobromic acid (50 ml) was boiled in presence of concentrated sulfuric acid (7 ml) for 6 hr. The product was purified by vacuum distillation and 25.6 g of octyl bromide was obtained (b.p. 63.5-65° at 3 mm; n_D^{20} 1.4502) [8].

Diethyl sebacate. Sebacic acid (30 g) was boiled with alcohol (60 ml) in presence of concentrated sulfuric acid (6 ml). The reaction mixture was worked up in the usual manner to give 30 g of diethyl sebacate with b.p. 158-159° at 7 mm, n_D^{20} 1.4382 [9].

Monoethyl sebacate [10]. Into a 250 ml round-bottomed flask, fitted with reflux condenser, were charged 40 g of sebacic acid, 30 g of its diethyl ester, 15 ml of n-dibutyl ether, and 7 ml of concentrated hydrochloric acid. The reaction mixture was heated on a metal bath (Wood alloy) to 160-170° with the objective of obtaining a homogeneous medium. The temperature was then lowered to 120-130°, and 15 ml of alcohol was added through the condenser. The solution was boiled for 2 hr. Towards the end of this period another 5 ml of alcohol was run in, and boiling continued for another 2 hr. After cooling, the reaction mixture was dried with sodium sulfate and fractionated in vacuo. 1st fraction (to 175° at 9 mm)—traces of alcohol and n-dibutyl ether; 2nd fraction (177-177.5° at 9 mm)—diethyl sebacate (40 g); 3rd fraction (196-196.5° at 6 mm)—monoethyl sebacate (25.6 g, m.p. 34-35°) [10].

Preparation of the acid chloride of monoethyl sebacate. To 25.6 g of monoethyl sebacate at room temperature was added 20 g of thionyl chloride. The reaction mixture was fractionated in vacuo to give 22 g of the acid chloride of the monoethyl ester of sebacic acid (b.p. 155-156.5° at 4 mm, n_D^{20} 1.4491) [11].

Synthesis of ethyl 10-ketooctadecanoate. A round-bottomed flask with a reflux condenser was charged with 26 g of octyl bromide in 100 ml of absolute ether and 3.4 g of dry magnesium. The flask was cooled with water and 15 g of anhydrous cadmium chloride was added in a single portion. The reaction mixture was stirred at room temperature for 1.5 hr, and then 28 g of the acid chloride of monoethyl sebacate was quickly added in ethereal solution. Heating and stirring were continued for another 4 hr, after which the reaction mixture was diluted with water. The reaction product was extracted with ether, the ether removed, and the residue fractionated in vacuo to give 20 g of ethyl 10-ketooctadecanoate (b.p. 202-203° at 7 mm, m.p. 41°) [6].

Preparation of 10-ketooctadecanoic acid. The ethyl ester (20 g) was hydrolyzed with 1 N alcoholic alkali. After recrystallization from alcohol, the product melted at 81° [12]. Yield 80%.

Found %: C 72.65, 72.61; H 11.43, 11.56. Acid number 190, 191.5. Number of OH groups 1.05, 1.09. $C_{18}H_{34}O_3$. Calculated %: C 72.43; H 11.48. Acid number 188. Number of OH groups 1.

No depression was observed in a mixed melting test on the 10-ketooctadecanoic acid with the acid obtained by oxidation of the diol.

Preparation of epoxypetroselinic acid. Peracetic acid in ethereal solution was used for oxidation of 100 g of petroselinic acid (m.p. 30°, iodine number 88). After recrystallization from alcohol the epoxy acid had m.p. 59-59.5° [13].

Reduction of epoxypetroselinic acid. The oxide (18.5 g) was reduced with lithium aluminum hydride (3.5 g) in a medium of absolute ether. The product was purified by recrystallization from alcohol and then from ligroine. M.p. 66-66.5°. Yield 80%.

Found %: C 75.26, 75.25; H 13.55, 13.34. Acid number 0. Number of OH groups 1.96, 1.97. $C_{18}H_{38}O_2$. Calculated %: C 75.46; H 13.37. Acid number 0. Number of OH groups 2.

Part of the octadecanediol (1.2 g) was chromatographed in a column filled with neutral aluminum oxide (100 g, 3rd activity). The compound was eluted with a mixture of ligroine and ether (1 : 8). The eluate was worked up in the usual manner and five fractions were collected: 1st 0.5 g m.p. 71°; 2nd 0.24 g, m.p. 69.5 °; 3rd 0.26 g, m.p. 69.5°; 4th 0.16 g, m.p. 69.5°; 5th 0.01 g, m.p. 71°. Mixed melting tests on each fraction with its neighbors did not give melting point depressions.

Oxidation of the diol. The octanediol (3 g) was oxidized by chromic acid (2.1 g) in acetic acid solution. The oxidation product, purified by recrystallization from alcohol, had m.p. 73.5-74.5° [14]. Yield 95%.

Found %: C 72.49, 72.41; H 11.53, 11.64. Acid number 188.8, 188.3. Number of OH groups 0.91, 0.89. $C_{18}H_{34}O_3$. Calculated %: C 72.43; H 11.48. Acid number 188. Number of OH groups 1.

Methyl hendecanoate. Hendecanoic acid (b.p. 141-142° at 6 mm; 30 g) [15], prepared by hydrogenation of undecylenic acid (b.p. 140-142° at 5 mm) [16] in absolute alcohol over palladium black, was esterified with methyl alcohol containing 20% gaseous hydrogen chloride. The ethereal solution of the products of methylation was worked up in the usual manner. After the ether had been removed, the compound was purified by vacuum distillation. A fraction (25 g) with b.p. 139-140° at 15 mm [17] was collected.

Preparation of hendecyl alcohol. Methyl hendecanoate (25 g) was reduced with lithium aluminum hydride (5.1 g) in ethereal solution. The reaction product was purified by vacuum distillation. A fraction was collected (19.5 g) with b.p. 122-123° at 10 mm, n_D^{20} 1.4394 [18].

Preparation of hendecyl bromide. A mixture of hendecyl alcohol (19 g) and 60% hydrobromic acid (26 ml) was boiled in presence of concentrated sulfuric acid for 6 hr. There was isolated 16.3 g of hendecyl bromide (b.p. 129-130.5° at 15 mm, n_D^{20} 1.4557) [19].

Diethyl pimelate [20] was prepared by boiling pimelic acid (30 g) with ethyl alcohol (72 ml) for 2 hr in presence of concentrated hydrochloric acid (7.2 ml). There was obtained 31 g of diethyl ester with b.p. 158-159° at 30 mm, n_D^{20} 1.4335.

Monoethyl ester of pimelic acid. Prepared by the method that we used for preparation of the monethyl ester of sebacic acid. Initial components were 39 g of pimelic acid, 30 g of its diethyl ester, 15 ml of n-butyl ether, 7 ml of concentrated hydrochloric acid, and 20 ml of ethyl alcohol. Vacuum distillation yielded the following fractions: 1st (to 125° at 2 mm)–ethyl alcohol and n-dibutyl ether; 2nd (125-127° at 2 mm)–diethyl pimelate (40 g); 3rd (145-148° at 2 mm)–monoethyl pimelate (22.5 g, n_D^{20} 1.4392) [21].

Preparation of acid chloride of monoethyl ester of pimelic acid. To 22.5 g of monoethyl ester was added at room temperature 16.4 g of thionyl chloride. The reaction mixture was then distilled in vacuo to give 19.95 g of the acid chloride (b.p. 128-129° at 17 mm, n_D^{20} 1.4451) [18].

Synthesis of ethyl 7-ketooctadecanoate was performed under the conditions described for ethyl 10-ketooctadecanoate. Reaction components were 16 g of hendecyl bromide, 1.7 g of dry magnesium, 7.5 g of anhydrous cadmium chloride, 14.05 g of acid chloride of monoethyl ester of pimelic acid. The reaction gave 16.65 g of ethyl 7-ketooctadecanoate with b.p. 199-203° at 7 mm, m.p. 37° [22].

Preparation of 7-ketooctadecanoic acid. The ethyl ester (5 g) was hydrolyzed by heating with 1 N alcoholic potassium hydroxide. After recrystallization from alcohol, the isolated ketoacid had m.p. 75.5-76.5° [14]. Yield 95%.

Found %: C 72.75, 72.71; H 11.58, 11.64. Acid number 187.5, 187.2. Number of OH groups 1.05, 1.02. $C_{18}H_{34}O_3$. Calculated %: C 72.43; H 11.48. Acid number 188. Number of OH groups 1.

No depression of melting point was found in a mixed test of 7-ketooctadecanoic acid with the ketooctadecanoic acid obtained by oxidation of the corresponding diol.

SUMMARY

Reduction with lithium aluminum hydride of the oxides of oleic and petroselinic acids gave 1,10-octadecanediol and 1,7-octadecanediol respectively. Opening of the oxide ring proceeds preferentially from the side of the carboxyl group.

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THE REACTION OF OXIDES OF HIGHER UNSATURATED ACIDS WITH LITHIUM ALUMINUM HYDRIDE

II. THE OXIDE OF METHYL ERUCATE

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In the preceding communication [1] we showed that reduction of the oxides of oleic and petroselinic acids by lithium aluminum hydride leads to 1,10-octadecanediol and 1,7-octadecanediol respectively. Under these conditions the oxide ring is opened from the side of the carboxyl group.

Our present communication is concerned with investigation of the reduction of the oxide of the methyl ester of eruic acid (cis-Δ^{13}-docosenoic acid). It was also shown that during this reaction the oxide ring is opened preferentially on one side, namely on the side of the ester group, and the reaction leads to formation of 1,14-docosanediol. The identity of the diol was demonstrated by chromatography. The position of the second hydroxyl group was verified by comparison of the properties of the ketodocosanoic acid obtained by oxidation of the diol with those of the 14-ketodocosanoic acid prepared by hydration of behenolic acid [2].

EXPERIMENTAL

Methylation of erucic acid. A mixture of 40 g of erucic acid (m.p. 34°, iodine number 74.8) [3, 4] and methyl alcohol (150 ml) was heated in presence of concentrated sulfuric acid (3.5 ml). The reaction product was distilled in vacuo and 38.6 g of methyl erucate was isolated (b.p. 228-230° at 10 mm, n_D^{20} 1.4550, iodine number 69.3) [5].

Preparation of the oxide of the methyl ester of erucic acid The ester (38.6 g) was oxidized with peracetic acid in ethereal solution. After recrystallization from alcohol, the oxide had m.p. 29-30°. Yield 76%.

Found %: O (epoxy) [6] 4.344, 4.336. $C_{23}H_{44}O_3$. Calculated %: O (epoxy) 4.34.

Preparation of 1,14-docosanediol. The oxide of the methyl ester of erucic acid (20 g) was reduced with lithium aluminum hydride (2.57 g) in a medium of anhydrous ether. The reduction product was purified by recrystallization from alcohol and had m.p. 80-80.5°. Yield 80%.

Found %: C 77.35, 77.37; H 13.53, 13.45. Acid number 0. Number of OH groups 1.98, 1.96. $C_{22}H_{46}O_2$. Calculated %: C 77.12; H 13.53. Acid number 0. Number of OH groups 2.

Part of the docosanediol (1.2 g) was chromatographed in a column packed with neutral alumina (100 g; 3rd activity). The substance was eluted with a mixture of ligroine and ether (1 : 9) and two fractions were collected: 1st, 1.12 g, m.p. 81.5-82°; 2nd 0.06 g, m.p. 81°. A mixture of the two fractions did not exhibit a melting point depression.

Isolation of ketobehenic acid. Docosanediol (6 g) was oxidized with chromic acid (2.34 g) in acetic acid solution at room solution. The separated ketoacid was recrystallized from alcohol and ligroine. M.p. 83.5-85° [2, 7]. Yield 85%.

Found %: C 74.51, 74.62; H 11.91, 12.08. Acid number 156, 156.9. Number of OH groups 0.93, 0.91. $C_{22}H_{42}O_3$. Calculated %: C 74.52; H 11.94. Acid number 158. Number of OH groups 1.

Semicarbazone of ketodocosanoic acid: m.p. 102-104°.

Found %: N 10.11, 10.08. $C_{23}H_{45}O_3N_3$. Calculated %: N 10.21.

Bromination of erucic acid. To a cooled ethereal solution of erucic acid (7.6 g) was added 1.3 ml of bromine. The bromination product was purified by recrystallization from ligroine. M.p. 44° [8]. Yield 85%.

Preparation of behenolic acid [9]. Erucic acid dibromide (9.55 g) was boiled with alcoholic potassium hydroxide (4.28 g in 30 ml alcohol) for 9 hr. The separated acid had m.p. 58° [8] (from alcohol).

Found %: C 78.42, 78.37; H 11.81, 11.88. Acid number 165, 165.7. $C_{22}H_{40}O_2$. Calculated %: C 78.51; H 11.98. Acid number 166.4.

Preparation of 14-ketodocosanoic acid. Behenolic acid (0.7 g) was hydrated with concentrated sulfuric acid (1 ml). A ketoacid was isolated, which after recrystallization from alcohol, had m.p. 83.5° [2, 7]. Yield 76%.

Found %: C 74.28, 74.48; H 11.96, 11.91. Acid number 159, 185.8. Number of OH groups 0.96, 0.98. $C_{22}H_{42}O_3$. Calculated %: C 74.52; H 11.94. Acid number 158. Number of OH groups 1.

A mixture of the 14-ketodocosanoic acid and ketodocosanoic acid prepared by oxidation of the diol did not suffer a depression of melting point.

Semicarbazone of 14-ketodocosanoic acid: m.p. 103-104°.

Found %: N 10.31, 10.27. $C_{23}H_{45}O_3N_3$. Calculated %: N 10.209.

A mixture with the semicarbazone of ketodocosanoic acid prepared by oxidation of the diol did not suffer a depression of melting point.

SUMMARY

1. Reduction of the oxide of the methyl ester of erucic acid with lithium aluminum hydride gave 1,14-docosanediol. Opening of the oxide ring proceeds preferentially from the side of the ester grouping.

2. Oxidation of the docosanediol with chromic acid gave 14-ketobehenic acid (14-keto-1-docosanoic acid).

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TRITERPENIC SAPONINS

I. SAPONINS FROM THE ROOTS OF Aralia Mandshurica

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Although triterpenic saponins have been known for a fairly long time, and in some instances possess very marked physiological activity [1-3], and are technically important, only conflicting data are available for their detailed structure. The structure of the aglucons of triterpenic saponins is generally known completely, but the hydrocarbon part of the molecule has only been studied partly or completely in isolated cases [2-4]. It is certain in this connection that no small part is played in the physiological activity of triterpenic saponins by the hydrocarbon component which appears to determine the specificity of the biological action.

Plants of the Araliaceae family—Aralia Mandshurica Rupr. et Max., Panax ginseng Meg., Echinopanax elatum, etc.—are known to possess a well-marked tonic activity, but nothing is known with certainty about the nature of the active principles of these plants. In this communication we submit the results of a study of the saponins of Aralia Mandshurica.

It was noted in a preliminary communication [5] that the saponins of Aralia Mandshurica are glycosides of oleanolic acid. The saponin fraction, obtained by treatment of the roots with methanol, contained a considerable admixture of phenolic substances and sugars. Serious difficulties were encountered in the separation of the saponins from these impurities and in particular from the carbohydrates. This problem was eventually solved most simply with the help of partition chromatography in the system n-butanol—ethanol—aqueous ammonia (see Experimental). This method of purification gave a mixture of saponins completely free of phenolic impurities and containing only a trace of carbohydrates. A more detailed paper chromatographic study of the total saponins obtained by this procedure showed that a mixture of several substances of similar character was present. We selected the following combinations after a systematic investigation of solvent systems for paper chromatography: n-butanol—ethanol—15% aqueous ammonia (18 : 3. 5 : 18 by volume, upper layer, system I*), n-butanol—water—acetic acid (4 : 5 : 1 by volume, upper layer, system II), and n-butanol—ethyl acetate—ethylene glycol (5 : 8 : 3 by volume, system III) [3]. The substances that we were investigating had the most convenient R_f values (0.4-0.8) in these systems. The saponins were detected on the paper chromatograms with the help of a solution of 15 g of antimony trichloride, 2 ml of antimony pentachloride, and 2 ml of thionyl chloride in 100 ml of chloroform. This reagent differed from the reagents described in the literature [6] in being very sensitive (it detected as little as 10-20 γ of saponin); after 2-3 min at 80° it colored the stain of the saponins (derivatives of oleanolic acid and their acetates as well as oleanolic acid and its acetate) a characteristic pink-lilac color which later changed to blue-violet.

Paper-chromatographic analysis revealed the presence in the saponin fraction of Aralia Mandshurica extract of three saponins which are fairly sharply separated in system I, although they could not be separated in systems II and III (Figs. 1-3).

We effected preliminary resolution of the mixture of saponins by partition chromatography in columns using system I as the mobile phase and cellulose (or alumina) as the carrier (stationary phase). Three saponins were thus isolated, and their chromatographic treatment on paper in the three systems (I, II, III) revealed their homogeneity and their separate identities (Figs. 1-3).

* This system is similar to one described earlier; compare [3].

In this manner we isolated the ammonium salts of the saponins, for which we propose the name of araloside A, araloside B, and araloside C. these are colorless, amorphous powders without definite melting points and decomposing at above 250°. They are readily soluble in water and in aqueous alcohol but completely insoluble in acetone and ether. A considerable residue of ash was obtained in empirical analysis of the ammonium salts of the saponins. The

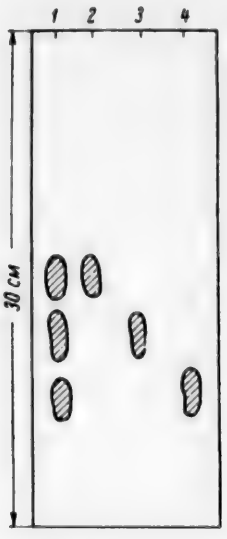

Fig. 1. Paper chromatogram of saponins of Aralia Mandshurica. Mobile phase: upper layer of mixture n-butanol–ethanol–15% aqueous ammonia (18 : 3.5 : 18). 1) Total saponins of the methyl alcohol extract of the roots; 2) araloside C, R_f 0.52; 3) araloside B, R_f 0.64; 4) araloside A, R_f 0.76.

Fig. 2. Paper chromatogram of saponins of Aralia Mandshurica. Mobile phase: upper layer of mixture n-butanol–water–acetic acid (4 : 5 : 1). 1) Total saponins of methanol extract of roots; 2) araloside C, R_f 0.52; 3) araloside B, R_f 0.60; 4) araloside A, R_f 0.78.

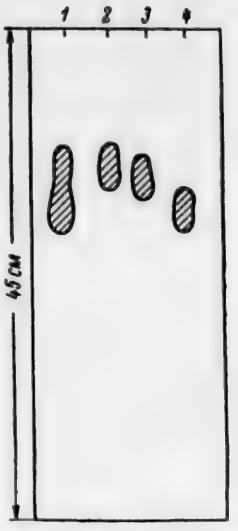

Fig. 3. Paper chromatogram of saponins of Aralia Mandshurica. Mobile phase: n-butanol–ethyl acetate–ethylene glycol (5 : 8 : 3). Paper impregnated with ethylene glycol. 1) Total saponins of methanol extract of roots; 2) araloside C, R_f 0.29; 3) araloside B, R_f 0.31; 4) araloside A, R_f 0.38.

inorganic impurities are very obstinately retained in the saponins. This greatly hindered investigation of acidic triterpenic saponins. It is evidently a characteristic property [7, 8]. For this reason we were unable to obtain definite empirical analytical data for the ammonium salts of the saponins. All three saponins were therefore converted into their full acetates by heating with acetic anhydride in pyridine. The acetates easily recrystallize from aqueous alcohol and form crystalline substances, although without definite melting points (they softened over a range of several degrees). Each of the acetates of aralosides A, B, and C was characterized by the specific rotatory power; they were resolved according to their R_f values on a paper chromatogram in the system xylene–chloroform–propylene glycol (Fig. 4). Empirical analysis of the acetates of aralosides A, B, and C gave results in full agreement with the values calculated for their composition as determined on the basis of the results of hydrolysis reported below.

We showed earlier [5] that hydrolysis of the unpurified total saponins of Aralia Mandshurica gives oleanolic acid. These preliminary data have now been amplified by hydrolysis of all of the three individual aralosides. Hydrolysis was most conveniently effected by heating for 2 hr in a mixture of acetic and hydrochloric acids. Under these conditions aralosides A, B, and C were hydrolyzed to sapogenins. Chromatography of the genins (aglucons) on paper in the system xylene–octane–propylene glycol (Fig. 5) revealed the presence in them of two substances, one of which had a R_f value corresponding to oleanolic acid, while the other was identified as its acetate. For confirmation of the identity of the aglucon of aralosides A, B, and C, the aglucon formed by hydrolysis of the saponin was further subjected to acetylation with acetic anhydride in pyridine; the product was a homogeneous substance completely identical in melting point and infrared spectrum (Fig. 6) with oleanolic acid acetate. We can therefore consider proven the presence in aralosides A, B, and C of the same aglucon (oleanolic acid). Hydrolysis of the saponins

Chromatographing of Total Saponins of Aralia Mandshurica

Fraction No.	Saponins	Weight of saponins (mg)
1-21	–	–
22-28	Araloside A	550
29-37	Mixture of aralosides A and B	290
38-56	Araloside B	370
57-83	Mixture of aralosides B and C	480
84-216	Araloside C	840
217-240	–	–

in a mixture of acetic and hydrochloric acids causes the split-off oleanolic acid to be partly acetylated. It should be noted that also under other hydrolytic conditions (heating of the saponins in an aqueous methanolic solution of hydrochloric acid) the aglucon is partly converted into a mixture of oleanolic acid and its ester.

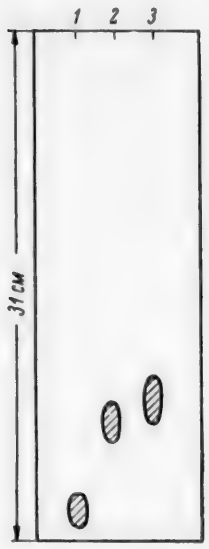

Fig. 4. Paper chromatogram of acetates of aralosides A, B, and C. Mobile phase: m-xylene–chloroform–propylene glycol. Paper impregnated with 1,2-propylene glycol. 1) araloside A acetate; 2) araloside B acetate; 3) araloside C acetate.

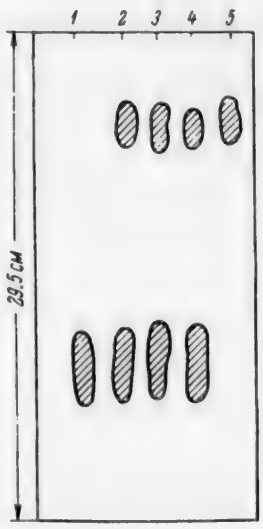

Fig. 5. Paper chromatogram of aglucons of aralosides A, B, and C. Mobile phase: m-xylene–n-octane–1,2-propylene glycol (1 : 1). Paper impregnated with 1,2-propylene glycol. 1) oleanolic acid acetate; 2,3,4) aglucons of aralosides A, B, and C; 5) oleanolic acid.

The hydrolytic data also clarified the nature of the carbohydrate portion of aralosides A, B, and C. The mother liquors from hydrolysis were paper chromatographed in the systems n-butanol–water–acetic acid (4 : 5 : 1), phenol–water, and phenol– 10% acetic acid. The presence of three monosaccharides in aralosides A and B was thereby established (Fig. 7), and they were identified (from the R_f value and the color developed with solutions of acid aniline phthalate or of p-anisidine phosphate) as glucose, arabinose, and glucuronolactone. The stains with the lowest R_f value did not correspond to glucuronic acid and were caused by a substance formed from glucuronic acid during hydrolysis of the saponin, since an authentic specimen of glucuronic acid (Fig. 7) under the same conditions gave a completely identical chromatogram.

Aralosides A and B consequently contain identical monosaccharides and differ only in the quantitative ratio of the monosaccharides. The ratio is established by analysis of the acetates of aralosides A and B. The analytical data for the full acetate of araloside A (see Experimental) correspond to the trioside of oleanolic acid, whereas the data for the full acetate of araloside B correspond to a tetroside containing glucose, arabinose, glucuronic acid, and (as the fourth sugar) arabinose or glucose.

In precisely similar manner it was established that hydrolysis of araloside C gives four monosaccharides (Fig. 7): glucose, xylose, glucuronic acid, and, apparently, galactose whose stain nearly merged with that of glucose when the above system of solvents was employed. Analysis of the full acetate of araloside C indicates the presence of a tetroside of oleanolic acid.

From the roots of Aralia Mandshurica we have thus isolated for the first time individual substances belonging to the class of triterpenic saponins. They were identified as glycosides of oleanolic acid of similar structures. It should be noted that the aralosides A, B, and C that we isolated are also very similar in structure to ginseng saponins;

according to Japanese workers [7], for example, one of the saponins of Panax repens (panax saponin), not isolated in the pure form, contains oleanolic acid, glucose, arabinose, and glucuronic acid.

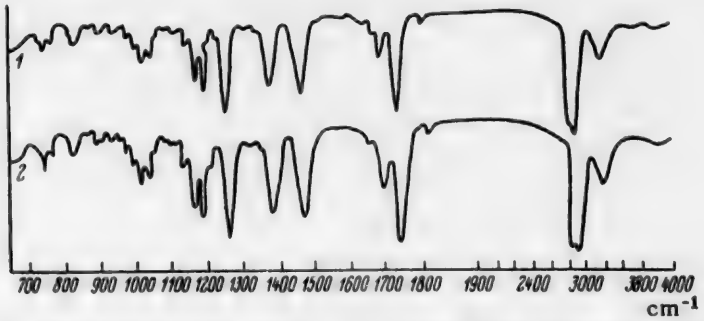

Fig. 6. Infrared absorption spectra. 1) Acetate of the aglucon of araloside A; 2) acetate of oleanolic acid.

EXPERIMENTAL

Chromatography was carried out on grade M chromatographic paper from the Leningrad works. Descending chromatograms were prepared.

Isolation and purification of the total saponins. A solution of 20 g of the methanol extract of Aralia Mandshurica [5] in 250 ml of solvent (system I) was prepared by stirring. The solution was filtered through a bed of alumina or cellulose (height 10-15 cm and diameter 10 cm), the adsorbent was then washed with the same solvent, and only those fractions of mother liquor that gave a positive color reaction for triterpenic saponins (reagent from $SbCl_3$, $SbCl_5$, $SOCl_2$) were collected. The solution containing the mixture of saponins (about 700-800 ml) was evaporated in vacuo, at a temperature not exceeding 60°, to a volume of 50-75 ml; the main bulk of the ammonium salts of the saponins came down in the form of a colorless or yellowish precipitate. The residue after evaporation was diluted with 150 ml of dry acetone. The total precipitated ammonium salts of the saponins were filtered, washed on the filter with dry acetone (3 x 100 ml), and dried in a vacuum-desiccator over phosphorus pentoxide. The mother liquor gave a negative reaction for saponins. The weight of the mixture of ammonium salts of saponins was 10-12 g. The total ammonium salts of the saponins obtained in this manner did not contain phenolic substances, and only traces of reducing sugars. It was subjected without further purification to chromatographic resolution.

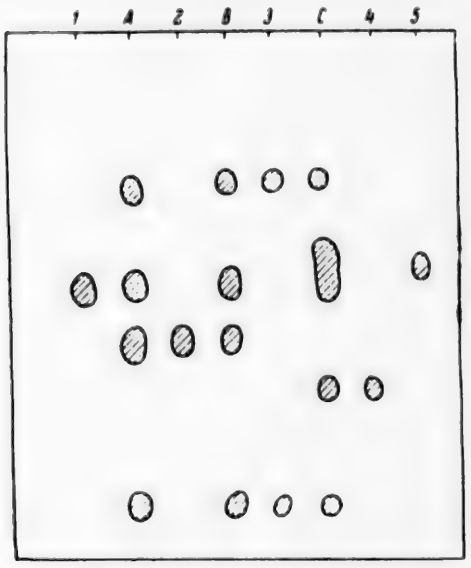

Fig. 7. Paper chromatogram of monosaccharides formed during hydrolysis of aralosides A, B, and C. Mobile phase: upper layer of mixture of n-butanol–water–acetic acid (4 : 5 : 1). 1) Glucose; 2) arabinose; 3) glucuronic acid after heating under conditions of hydrolysis of the saponins; 4) xylose; 5) galactose; A) Araloside A; B) araloside B; C) araloside C.

Chromatographic resolution of the total saponins. The total ammonium salts of the saponins (3.0 g) was chromatographed on 600 g of alumina or 250-300 g of cellulose (height 730 mm, diameter 35 mm) in system I, fractions being collected by an automatic fractionating apparatus. A total of 240 fractions (8 ml each) was collected (see Table).

Fractions containing single saponins were evaporated to a small volume in vacuo at a temperature not exceeding 60°. The precipitated saponin salts were filtered, washed on the

filter with a small volume of cold butanol, and then with dry acetone. Specimens for analysis were dried in high vacuum (10^{-5}mm) at room temperature for 3-4 hr.

The ammonium salt of araloside A was a colorless, amorphous powder decomposing above 290°, readily soluble in water, aqueous butanol, methanol, ethanol, and pyridine, insoluble in anhydrous ethanol, butanol, and acetone.

Found %: C 57.59, 57.30; H 8.30, 8.45. Residue of ash 4.34, 3.90%.

The ammonium salt of araloside C was a colorless, amorphous powder decomposing at above 260°, readily soluble in water, aqueous alcohol, and pyridine, insoluble in butanol and acetone.

Found %: C 54.01, 53.92; H 7.79, 7.74. Residue of ash 6.02, 5.80%.

Acetate of araloside A. To a solution of 97.6 mg of ammonium salt of saponin A in 3 ml of anhydrous pyridine was added 1 ml of acetic anhydride, and the mixture allowed to stand at room temperature for 48 hr. The reaction mixture was then poured into water, and the colorless precipitate filtered and dried in vacuo over phosphorus pentoxide. Yield 115 mg. An analytical specimen of the acetate of araloside A was obtained by one recrystallization from 90% ethanol and drying in high vacuum (4×10^{-5}mm) at room temperature. The compound softens at 135-144°; $[\alpha]_D^{20}$ -40° (c 0.68; ethanol). Soluble in butanol, chloroform, and acetone, sparingly soluble in aqueous alcohol.

Found %: C 60.21, 60.22; H 7.18, 7.15. $C_{63}H_{88}O_{26}$. Calculated %: C 59.98; H 7.03.

Acetates of aralosides B and C were similarly prepared. The acetate of araloside B melts at 132-140°; $[\alpha]_D^{20}$ -16° (c 2.61; acetone).

Found %: C 58.56, 58.58; H 7.02, 6.84.

The acetate of araloside C melts at 133-141°; $[\alpha]_D^{20}$ -1° (c 2.13; ethanol).

Found %: C 58.48, 58.35; H 6.95, 6.85, 6.85.

Calculated % for acetates of aralosides B and C: a) reckoned on the full acetate of the tetroside containing 2 moles of pentose, 1 mole of hexose, and 1 mole of hexuronic acid ($C_{72}H_{100}O_{32}$), C 58.53; H 6.82; b) reckoned on the full acetate of the tetroside containing 2 moles of hexose, 1 mole of pentose, and 1 mole of hexuronic acid ($C_{75}H_{104}O_{34}$), C 58.13; H 6.77; c) reckoned on the full acetate of the tetroside containing 2 moles of hexuronic acid, 1 mole of pentose, and 1 mole of hexose ($C_{73}H_{100}O_{34}$), C 57.61; H 6.63.

Hydrolysis of araloside A. Ammonium salt of araloside A (110.9 mg) was dissolved in 4 ml of a mixture of acetic acid–concentrated hydrochloric acid–water (35 : 10 : 55 by volume) and the solution was boiled for 2 hr. The precipitated sapogenin was separated from the solution, washed with distilled water, and dried in vacuo over phosphorus pentoxide. Yield of aglucon 50.7 mg with m.p. 235-237°. The aglucon is a mixture of oleanolic acid and its acetate (see Fig. 5). A mixture of 34.3 mg of aglucon and 0.1 ml of acetic anhydride was boiled in 1 ml of pyridine, the cooled reaction mixture was diluted with water, and the precipitated aglucon acetate filtered and recrystallized from alcohol. M.p. 259-260°; a mixture with authentic acetate of oleanolic acid did not exhibit a melting point depression. Both specimens also had the same infrared spectra (Fig. 6). The mother liquor from the sapogenin was subject to a paper-chromatographic analysis. The monosaccharides detected by this technique were identified as glucose, arabinose, and glucuronic acid (Fig. 7).

Hydrolysis of araloside B was carried out by the above procedure. The resulting aglucon was fully identical with that obtained by hydrolysis of araloside A, i.e., it was a mixture of oleanolic acid and its acetate as was demonstrated by paper chromatography (Fig. 5). As previously, chromatographic examination of the mother liquor from the aglucon revealed the presence of glucose, arabinose, and glucuronic acid (Fig. 7).

Hydrolysis of araloside C was performed as in the two preceding cases. The resulting aglucon was a mixture of oleanolic acid and its acetate (Fig. 5). Paper chromatographic analysis of the mother liquor, carried out as above, showed the presence of xylose, glucuronic acid and glucose; the stain of the latter nearly merged with the stain corresponding to galactose, which closely resembles the glucose stain in size and in color (Fig. 7).

SUMMARY

1. From the roots of Aralia Mandshurica Rupr. er Max. was isolated a mixture of triterpenic saponins which was further resolved by partition chromatography into three individual saponins–araloside A, araloside B, and araloside C. These were characterized in the form of their full acetates.

2. It was established by hydrolysis that all three araloside contain oleanolic acid as the aglucon. Araloside A is a trioside containing one residue each of glucose, arabinose, and glucuronic acid; araloside B is a tetroside containing a glucose, arabinose, and glucuronic acid residue, together with glucose or arabinose as the fourth monosaccharide; araloside C is a tetroside constituted from glucose, arabinose, glucuronic acid, and, apparently, galactose.

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A NEW METHOD OF PREPARATION OF CIS-CYCLOBUTANE-1,2-DICARBOXYLIC ACID

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Cyclobutane-1,2-dicarboxylic acid (IV) (in the form of a mixture of cis- and trans-forms) was first obtained by decarboxylation of cyclobutane-1,1,2,2-tetracarboxylic acid [1]. The ester of the latter (III) was prepared by the action of bromine on the disodium derivative of the ester of butane-1,1,4,4-tetracarboxylic acid [1-4].

The same mixture of stereoisomeric cyclobutane-1,2-dicarboxylic acids was prepared by decarboxylation of cyclobutane-1,1,2-tricarboxylic acid, which in turn was prepared by the action of sodium cyanide [5] or potassium cyanide [6, 7] on the ester of 2,5-dibromoadipic acid.

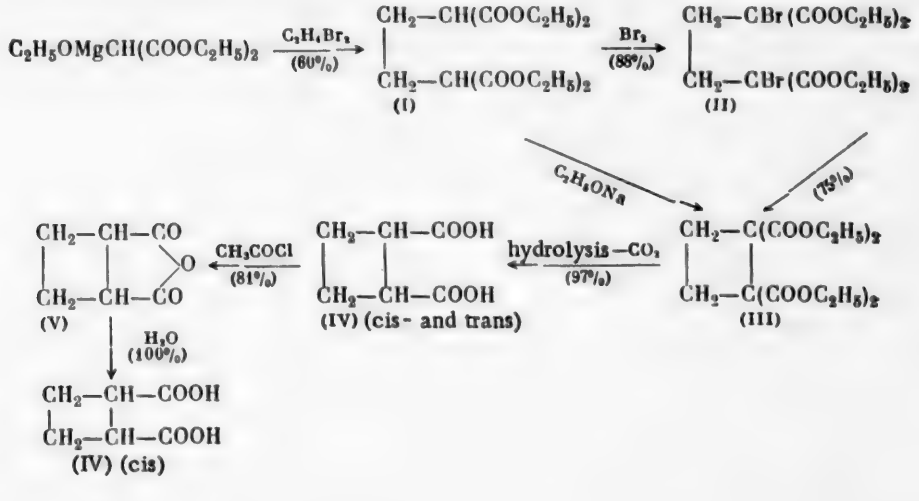
Pure cis-acid (IV) is obtained by treating the above mixture of acids with acetyl chloride; the cis-acid forms the cyclic anhydride (V) [1], while the trans-acid forms a mixed anhydride with acetic acid which breaks down on heating to 175° to the anhydride of the cis-acid (V) and acetic anhydride [7]. The anhydride of the cis-acid is converted to the cis-acid by boiling with water [1, 7].

Finally, cis-cyclobutane-1,2-dicarboxylic acid can be obtained by oxidation of cyclooctatetraene dichloride followed by dehalogenation of the resulting cis-3,4-dichlorocyclobutane-1,2-dicarboxylic acid [8].

The last two methods are usually employed for small-scale preparation of cis-cyclobutane-1,2-dicarboxylic acid.

Another route to the ester of cyclobutane-1,1,2,2-tetracarboxylic acid (III) is described in the literature. It involves the action of disodium butane-1,1,4,4-tetracarboxylic ester on 1,4-dibromobutane-1,1,4,4-tetracarboxylic ester [9].

In the present work we attempted to apply this reaction to laboratory preparation of cis-cyclobutane-1,2-dicarboxylic acid (IV). We modernized the previous recipe for preparation of large quantities, introduced a series of improvements, and developed an extremely simple and convenient method of preparation of cis-cyclobutane-1,2-dicarboxylic acid comprising the following steps:



However the exploitation of this method was hindered by the lack of a satisfactory route to the initial ester of butane-1,1,4,4-tetracarboxylic acid (I). Reaction of sodium malonic ester with ethylene bromide [1] or chloride [1, 10] gives very low yields (3% and 30% respectively), while the method using magnesium malonic ester [11] is too inconvenient due to the need to prepare the latter via magnesium amalgam; moreover it leads to butane-1,1,4,4-tetracarboxylic ester heavily contaminated (up to 5%) with the ester of cyclohexane-1,1,4,4-tetracarboxylic acid [12, 13].

Our experiments showed that the ester of butane-1,1,4,4-tetracarboxylic acid (I) is obtained in 60% yield by reaction of ethylene bromide with ethoxymagnesiummalonic ester prepared by the method of Lund [14]. It is contaminated with only 1.4% of the ester of cyclohexane-1,1,4,4-tetracarboxylic acid if the equivalent amount of metallic magnesium is used, and not an excess (as in earlier work [11-13]).

The proposed method was tried out for preparation of over 800 g of cis-cyclobutane-1,2-dicarboxylic anhydride (V). It differs from earlier methods in being simple in operation, in starting from accessible substances [8], in not requiring the use of cyanides [5], and in immediately giving a sufficiently pure cyclobutane-1,1,2,2-tetracarboxylic acid (IV), which does not need to be converted to the lead [1] or barium [3] salt.

The total yield of cis-cyclobutane-1,2-dicarboxylic acid was 30%, calculated on the malonic ester.

EXPERIMENTAL

Butane-1,1,4,4-tetracarboxylic ester (I). Into a flask of 3 liters capacity, equipped with dropping funnel and reflux condenser topped by a calcium chloride tube, were charged 36 g of magnesium turnings and about 100 ml of a mixture prepared from 480 g of malonic ester, 550 ml of absolute alcohol, and 5 ml of CCl_4. The flask was heated with a smoky flame until a vigorous reaction commenced, whereupon the remainder of the mixture was added at such a rate that the mass boiled uniformly. After the whole of the magnesium had dissolved, the liquid was cooled slightly, 282 g of ethylene bromide was added in a single portion, and the mass heated for 9 hr on an oil bath (about 120°). The cooled mass was then decomposed with 1500 ml of 15% H_2SO_4, the layer of reaction products collected, the aqueous layer extracted three times with ether, and the ethereal extracts combined with the main mass of products. After three washings with water and drying with $CaCl_2$, the ether was driven off and the residue fractionated in vacuo to give an average of 100 g (35.4% reckoned on the initial quantity) of ethylene bromide with b.p. 70-71° at 40 mm, 180 g (37.5%) of malonic ester, and 200-220 g of impure butanetetracarboxylic ester with b.p. 189-200° at 4 mm.

Redistillation of the product from 18 experiments led to collection of 3529 g of pure butanetetracarboxylic ester with b.p. 175-176° at 2 mm. Since the recovered malonic ester was reused in later experiments with addition of the balance of the substance, the yield was 60.4%.

d_4^{20} 1.1094, n_D^{20} 1.4428, MR_D 82.62; calc. 82.70.

After prolonged storage the butanetetracarboxylic ester did not deposit crystals of ester of cyclohexane-1,1,4,4-tetracarboxylic acid [12], and only faint cloudiness was developed.

1,4-Dibromobutane-1,1,4,4-tetracarboxylic ester (II). A 1.5 liter flask, equipped with mechanical stirrer, dropping funnel and reflux condenser, was charged with 346 g of ester (I) dissolved in 670 ml of chloroform. Addition was then made, with ice water cooling, of 105 ml of dry bromine in the course of 1.5-2 hr. After completion of the addition, the flask was heated on a water bath for 5 hr at 50° and for 1 hr at 70°. The chloroform and excess bromine were then distilled off (about 550 ml), and the residue was transferred to a porcelain dish and evaporated on a water bath. The residue in the dish crystallized on cooling. The crystals were transferred to a funnel with a glass filter and washed in two portions with 200 ml of alcohol cooled with ice water. About 440 g of product suitable for further work was obtained in this way. Evaporation of the wash alcohol yielded a further small quantity of dibromoester (II). From a total of 1875 g of butanetetracarboxylic ester was obtained 2401 g (87.9%) of the ester of 1,4-dibromobutane-1,1,4,4-tetracarboxylic acid (II) with m.p. 84° [15] (twice from alcohol).

Ester of cyclobutane-1,1,2,2-tetracarboxylic acid (III). To a solution of sodium ethoxide, prepared from 23 g of sodium and 500 ml of absolute alcohol, was added 175 g of (I). To the resulting yellow solution was added 252 g of ester (II) and the mixture heated on an oil bath (110-115°) for 4 hr. After cooling, the darkened reaction mixture was put into 1.5 liters of water acidified with a few drops of sulfuric acid. The layer of reaction products was separated and the aqueous layer extracted four times with ether (200 ml each time). The extracts were added to the main bulk of reaction products which was then washed four times with water (300 ml each time) and dried with $CaCl_2$.

The ether was driven off and the residue distilled in vacuo where nearly the whole of the material came over at 153-170° (2 mm). Redistillation of the fractions collected during working-up of 1654 g of tetracarboxylic ester gave 2436 g of cyclobutanetetracarboxylic ester (III) with b.p. 148-150° (1 mm), and 60 g of a fraction with b.p. 151-170°, from which on standing for 24 hr was isolated 22.8 g (1.4%) of the ester of cyclohexane-1,1,4,4-tetracarboxylic acid with m.p. 75-76°. Total yield of ester (III) 2473 g (75.2%).

d_4^{20} 1.1405, n_D^{20} 1.4509, MR_D 81.19; calc. 80.96.

Mixture of cis- and trans-cyclobutane-1,2-dicarboxylic acids (IV). A mixture of 488 g of ester (III) and 2 liters of hydrochloric acid (1 : 1) was boiled on an oil bath (130-140°) until the oily layer dissolved (35-40 hr). The hydrochloric acid was distilled at the ordinary pressure on an oil bath, and the residue heated at 180-200° until CO_2 ceased to be evolved. The residue crystallized completely. The yield of product with m.p. 102-104° was 280.8 g (97.5%).

Anhydride of cis-cyclobutane-1,2-dicarboxylic acid (V). A mixture of 288 g of mixed cyclobutane-1,2-dicarboxylic acids and 1 kg of acetyl chloride was put into a 1.5 liter flask and refluxed on a water bath at 70-90° for 5 hr. The excess of acetyl chloride and the resulting acetic acid were distilled at the usual pressure, and the residue was heated on an oil bath at 160-175° for 6-7 hr. This treatment led to decomposition of the mixed anhydride of trans-cyclobutane-1,2-dicarboxylic and acetic acids. The residue was fractionated in vacuo; at 50 mm about 110 g of acetic anhydride came over; this was followed at 2 mm and 113-114° by 203-205 g of the anhydride of cis-cyclobutane-1,2-dicarboxylic acid, which at once crystallized. Redistillation gave a product boiling at 108-110° (1 mm). Yield of anhydride with m.p. 78° was 716 g (81.2%).

Boiling of anhydride (V) with double the quantity of water and subsequent evaporation on the water bath led to quantitative conversion to cis-cyclobutane-1,2-dicarboxylic acid, which after recrystallization from water melted at 137-138° [1].

SUMMARY

1. A convenient preparative method was developed for cis-cyclobutane-1,2-dicarboxylic acid and its anhydride which consisted in reaction of the disodium derivative of butane-1,1,4,4-tetracarboxylic ester with 1,4-dibromobutane-1,1,4,4-tetracarboxylic ester followed by acidic hydrolysis of the resulting ester of cyclobutane-1,1,2,2-tetracarboxylic ester, decarboxylation, and conversion of the mixture of cis- and trans-cyclobutane-1,2-dicarboxylic acids into the anhydride of cis-cyclobutane-1,2-dicarboxylic acid by the action of acetyl chloride.

2. A new method was proposed for preparation of butane-1,1,4,4-tetracarboxylic ester, based on treatment of ethoxymagnesiummalonic ester with ethylene bromide.

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AN INVESTIGATION IN THE FIELD OF THE TERPENYLPHENOLS

IV. A STUDY OF THE PRODUCTS OF THE CONDENSATION OF CAMPHENE WITH o-CRESOL

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The usefulness of the terpenylphenols for the synthesis of new odoriferous substances has already been placed in perspective in the preceding communications [1-3].

Isobornyl-2-methylcyclohexanone, which possesses an exceptionally strong and distinctive odor, was earlier obtained by hydrogenation of the product of the condensation of camphene with o-cresol and subsequent oxidation of the cyclic alcohol thereby formed [4]. This synthesis has been realized recently on a production scale, and the ketone itself, under the name "musteron," has found application in perfumery as a replacement for expensive natural musk preparations [5].

However, "musteron" does not appear to be an individual compound, but acts like a mixture of isomeric ketones, which possibly possess different odors.

In establishing the composition of "musteron" it appeared interesting to us to study in greater detail the structure of the separate products which are obtained by the condensation of camphene with o-cresol in the presence of BF_3 in glacial acetic acid, and also to separate these products in pure form and to ascertain in what quantities they are formed.

In appearance, the product of the condensation of camphene with o-cresol is a very viscous oily substance which does not crystallize even upon many months of standing, and which, like the product of the condensation of camphene with phenol [3], is apparently a mixture of various isomers.

In the condensation of camphene with o-cresol the terpene substituent can enter into positions ortho and para to the hydroxyl group of the o-cresol. As a consequence of the strong steric hindrance which is created by the isobornyl group in the o-position to the hydroxyl, 2-methyl-6-isobornylphenol, like 2-isobornylphenol [3], must be considerably more difficult to dissolve in alkali than is the second possible isomer, 2-methyl-4-isobornylphenol.

We succeeded in isolating both possible isomers by applying our procedure to their separation; this consists in the treatment of the condensation products with an aqueous-alcoholic solution of caustic potash (containing approximately 30% of the quantity of KOH necessary for the conversion of all of the condensation product into the phenolate [3]).

2-Methyl-4-isobornylphenol, as was expected, was found in the form of the phenolate in the aqueous-alcoholic layer, and 2-methyl-6-isobornylphenol was easily separated from it by extraction with petroleum ether.

Both isomers solidified after several days, and following recrystallization from isopentane at a low temperature were obtained in the form of colorless crystalline substances with sharp melting points, sample mixtures both of the isomers themselves and of their 3,5-dinitrobenzoates giving noticeable melting point depressions.

The structure of the isomers was evinced by comparison of the infrared spectra of both substances in the regions of the composite frequencies (1700-2000 cm^{-1}), of the nonplanar deformation vibrations of the C–H bond (700-900 cm^{-1}) and of the valence O–H vibrations (approximately 3500 cm^{-1}).

The characteristic appearance of the spectrum of 2-methyl-4-isobornylphenol in the region of composite frequencies,and also the presence of the characteristic bands at 1508, 814 and 799 cm^{-1} clearly demonstrate the 1,2,4-positions of the substituents in the molecule of this isomer [6].

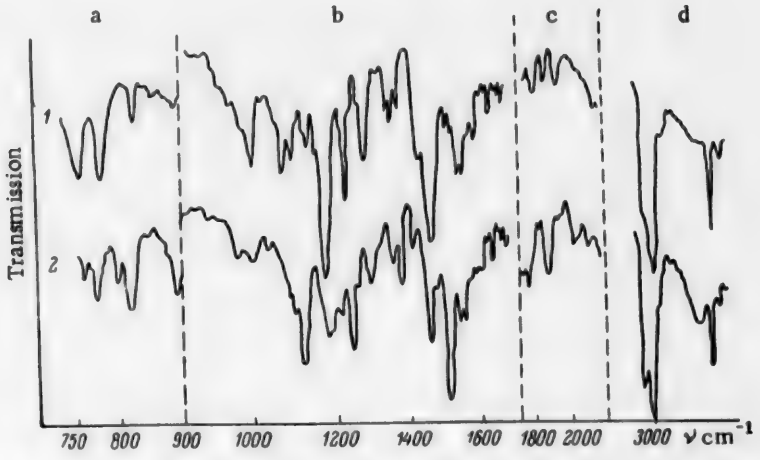


Fig. 1. Infrared absorption spectra. 1) 2-Methyl-6-isobornylphenol; 2) 2-methyl-4-isobornylphenol. a) In $CHBr_3$ solution; b) in CCl_4 solution; c) in $CHBr_3$ solution; d) in CCl_4 solution.

The positions of the substituents in the molecule of 2-methyl-6-isobornylphenol were confirmed by the appearance of the spectrum in the region of composite frequencies, which was typical of a 1,2,3-trisubstituted benzene; also by the presence of strong bands at 1470, 776 and 751 cm^{-1} [6]. The presence of a band of medium intensity at 823 cm^{-1} in the spectrum of 2-methyl-6-isobornylphenol should be mentioned; this was observed earlier by us in the spectrum of 2-isobornylphenol [3], and also in the spectra cited in the literature for 2-cyclohexylphenol, 2-methyl-6-cyclohexylphenol and 2-methyl-6-tert-butylphenol [7].

In the region of the valence O—H vibrations in the spectrum of 2-methyl-4-isobornylphenol, in addition to the bands of the monomers (approx. 3600 cm^{-1}) there was observed a broad and intense band of the associated molecules. In the spectrum of 2-methyl-6-isobornylphenol the bands of the monomer were considerably more intense, and the bands of the associated molecules were barely discernable, which was to be expected, considering the strong steric hindrance for the formation of intermolecular hydrogen bonds which is created by the isobornyl constituent in the ortho position to the hydroxyl.

The characteristic splitting of the bands of the symmetrical deformation vibration of the CH_3 group in the 1380 cm^{-1} region bears witness to the presence in the molecules of both isomers of gemdimethyl groups (doublets at 1389, 1366 cm^{-1} in the spectrum of 2-methyl-4-isobornylphenol,and 1396, 1372 cm^{-1} in the spectrum of 2-methyl-6-isobornylphenol), and also of the isolated CH_3 groups (band at 1376 and 1382 cm^{-1}).

Having preparations of both isomers, we were able to determine their quantities in the intial condensation product. A quantitative analysis was carried out based on the intensities of the maxima of the bands at 1508 and 799 cm^{-1} for 2-methyl-4-isobornylphenol,and the bands at 776 and 751 cm^{-1} for 2-methyl-6-isobornylphenol (taking into account the positions of the spectra of the isomers).

In this way it was established that there is contained in the intial condensation product 63-64% of 2-methyl-6-isobornylphenol and 35-37% 2-methyl-4-isobornylphenol. Thus the ratio between these isomers is 1.9 : 1, while in the alkylation of phenol by camphene under these same conditions, the ratio between the ortho- and para-isomers is considerably higher (3.5 : 1) [3]; this apparently depends in the case of phenol on the possibility of alkylation in both free o-positions.

Judging from the infrared spectra, in addition to the indicated isomers the condensation product of camphene and o-cresol contains approximately 5% of o-bornyl acetate (the band at 1737 cm^{-1}), which is formed apparently as a result of the acetylation of camphene by acetic acid in the presence of BF_3.

The ultraviolet spectrum of 2-methyl-4-isobornylphenol has two characteristic absorption maxima at about 280 and 230 mμ and a characteristic absorption minimum at about 252 mμ, while in the spectrum of 2-methyl-6-isobornylphenol the minimum of absorption is displaced to the shorter wavelength region (243 mμ); one of the maxima is found at about 274 mμ, and the second obviously also has moved into the shorter wavelength zone in a region not accessible to our instrument. An analogous regularity was also observed by us earlier in the ultraviolet spectra of p- and o-isobornylphenols [3].

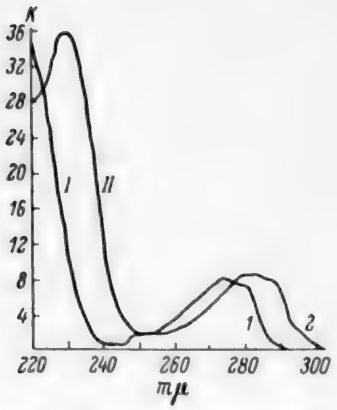
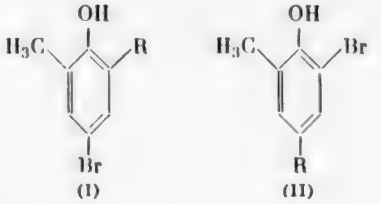


Fig. 2. Ultraviolet absorption spectra. 1) 2-Methyl-6-isobornylphenol; 2) 2-methyl-4-isobornylphenol. (The values K relate to the concentrations, expressed in grams/liter).

It is possible that a similar difference in the ultraviolet spectra is normal for p- and o-alkylphenols with bulky substituents; however, for a definitive conclusion additional spectral study of other analogous p- and o-alkyphenols is necessary.

The structure of the isomers isolated by us was confirmed also by the determination of the dipole moments* of their monobromo derivatives. Since the dipole moment of p-bromophenol (2.13 D) is significantly greater than the dipole moment of o-bromophenol (1.36 D) [8], we assumed that the dipole moment of the bromide (I), which appears to be a dialkyl derivative of p-bromophenol, also must be substantially greater than the dipole moment of the bromide (II), which apparently is a dialkyl derivative of o-bromophenol. The measured values of the dipole moments of the bromides (I) and (II) (2.80 and 1.84 D respectively) completely confirm our assumption and serve as yet another proof of structure of both the bromides and the initial isomers. The dipole moments of 2-methyl-4-isobornylphenol and 2-methyl-6-isobornylphenol are insignificantly different one from the other and are equal respectively to 1.46 and 1.44 D.



Because the spectral method of quantitative determination of the isomeric composition of the condensation product of camphene with o-cresol is rather complex and laborious we made an attempt to work out a simpler and more rapid method for the quantitative determination of the isomeric isobornyl-o-cresols.

Very encouraging results were obtained earlier with the help of the method of high-frequency titration for the determination of the total quantity of phenols and cresols in industrial products [9], and also for the determination of the content of the individual isomers in mixtures of o-, m-, and p-cresols [10].

With the purpose of testing the applicability of this method for the quantitative determination of the isobornyl-o-cresols, the individual isomers and also several artificial mixtures with different contents of these isomers were titrated. An aliquot of the substance was dissolved in acetone; this was treated with an excess quantity of alcoholic caustic potash, and the solution was titrated with an alcoholic solution of hydrochloric acid. Satisfactory results were obtained in all cases.

* The measurement of the dipole moments was carried out in the Faculty of Physical Chemistry of the Moscow Institute of Fine Chemical Technology by V. M. Kazakova and I. Yu. Kokoreva, to whom we express our sincere gratitude.

The amounts of 2-methyl-4-isobornylphenol and 2-methyl-6-isobornylphenol found by high-frequency titration in the condensation product were respectively 33-34 and 66-67%, which agrees very well with the data of the spectral analysis.*

It should be observed that for a high-frequency titration a very small quantity of the substance is required, and that the determinations themselves are exceptionally simple and take only minutes. The results of these first experiments with high-frequency titration give every reason to assume that further careful study of this question will lead to the development of a simple and sensitive method suitable for the quantitative determination of various alkylphenols.

EXPERIMENTAL

The condensation of camphene with o-cresol. To a stirred mixture of 270 g of o-cresol and 136 g of camphene at 25° there was gradually added during the course of 1 hour 6.2 g of a 34% solution of BF_3 in glacial acetic acid; the mixing was continued for 1 hour at 25°, 1 hour at 40°, 2 hours at 80° and 4 hours at 95-100°. The cooled reaction mixture was washed thoroughly first with soda salt, and then with salt solution until a neutral reaction was obtained to remove the excess o-cresol; the residue was distilled in vacuo. A light yellow oily condensation product was obtained. The yield was 65%, b.p. 150-155° at 1.5 mm, d_D^{20} 1.0273, n_D^{20} 1.5455.

The separation of the product of condensation into isomers. The oily condensation product was dissolved in a 2% aqueous-alcoholic solution of caustic potash. The quantity of KOH was approximately 30% of the quantity necessary for the conversion of all of the condensation product into the phenylate, and approximately corresponded to the amount of p-isomer in the condensation product. The solution obtained was extracted with petroleum ether; the basic, aqueous-alcoholic layer was separated and acidified by the addition of hydrochloric acid. The precipitated oil was dissolved in petroleum ether; the solution was washed thoroughly with water, dried with sodium sulfate, and the solvent was removed; the residue was distilled in vacuo. A yellow oil was obtained, b.p. 155-157° at 2 mm (n_D^{20} 1.5496), which on standing crystallized during the course of 2 or 3 days. After numerous recrystallizations from isopentane at a temperature of -10 to -20°, colorless crystals of 2-methyl-4-isobornylphenol were obtained with m.p. 93.5-95°. The phenol content was 98.7%.

Found %: C 83.74, 83.76; H 9.83, 10.12. Bromine number 65.8. $C_{17}H_{24}O$. Calculated %: C 83.55; H 9.90. Bromine number 65.5.

The benzoate – colorlorless crystals with m.p. 103.0-103.5° (from alcohol).

Found %: C 82.60, 82.84; H 7.96, 8.09. $C_{24}H_{28}O_2$. Calculated %: C 82.72; H 8.10.

3,5-dinitrobenzoate – crystals tinged with yellow with m.p. 171-172° (from methyl alcohol and chloroform, 3 : 1 by volume).

Found %: N 6.15, 6.11. $C_{24}H_{26}O_6N_2$. Calculated %: N 6.30.

The petroleum ether solution, which contained the isomer that had not reacted with the base was washed with water, dried with sodium sulfate and distilled in vacuo. A light yellow oil was obtained with b.p. 156-158° at 1.5 mm and (n_D^{20} 1.5436), which crystallized on standing in the course of several days. By recrystallization from isopentane at -20° there were obtained colorless crystals of 2-methyl-6-isobornylphenol with m.p. 54-55°. The phenol content was approximately 100%.

Found %: C 83.34, 83.66; H 10.0, 9.74. Bromine number 67.5. $C_{17}H_{24}O$. Calculated %: C 83.55; H 9.90. Bromine number 65.5.

A sample of a mixture of both isomers melted at 37-40°.

The benzoate – a noncrystalline light yellow oil.

The 3,5-dinitrobenzoate – colorless crystals with m.p. 119-120° (from methyl alcohol and chloroform, 3 : 1 by volume).

Found %: N 6.29, 6.42. $C_{24}H_{26}O_6N_2$. Calculated %: N 6.39.

* All determinations by high-frequency titration were performed in the Analytical Laboratory of the Scientific-Research Institute of Plastics by B. P. Ershov and S. P. Dvuglov, to whom the authors express their deep gratitude.

Obtaining the monobromo derivative of 2-methyl-4-isobornylphenol. In 50 ml of a 2 N solution of bromine in methyl alcohol, saturated with sodium bromide, was dissolved 5 g of 2-methyl-4-isobornylphenol; the mixture was left in darkness for 1.5 hours, after which an excess of a 10% solution of KI was added; the reaction mixture was treated with a 10% solution of sodium thiosulfate until there was decolorization of the evolved iodine. The brown precipitate was dissolved in isopentane, washed thoroughly with water and left to stand until the solvent had completely evaporated. After numerous recrystallizations of the residue from isopentane at -25° there were obtained colorless crystals of 2-methyl-4-isobornyl-6-bromophenol with m.p. 91-92°.

Found %: Br 24.62, 25.0. $C_{17}H_{23}OBr$. Calculated %: Br 24.72.

The monobromo derivative of 2-methyl-6-isobornylphenol was obtained by analogous procedures. After numerous recrystallizations from isopentane at -10° there was obtained 2-methyl-6-isobornyl-4-bromophenol in the form of colorless crystals with m.p. 104.5-105.5°.

Found %: Br 24.87, 24.82. $C_{17}H_{23}OBr$. Calculated %: Br 24.72.

The spectral measurements. The infrared spectra were measured with a single beam spectrometer with a NaCl prism. To obtain spectra in the regions 700-900 cm^{-1} and 1700-2000 cm^{-1}, $CHBr_3$ solutions of the substances under investigation were used—in the 900-1700 cm^{-1} and 3500 cm^{-1} spectral regions, solutions in CCl_4. The ultraviolet absorption spectra were measured in a SF-4 spectrophotometer in alcohol solution.

SUMMARY

1. It was shown that the alkylation of o-cresol by camphene in the presence of boron trifluoride occurs in the o- and p-positions to the hydroxyl.

2. A method was devised for the separation of the isomers formed which allowed the isolation of these isomers in pure form from the products of the condensation.

3. The position of the terpene substituent in the isolated crystalline isomers was strictly demonstrated with the help of the infrared spectra and also by the measurement of the dipole moments of the monobromo derivatives of both isomers.

4. With the help of the infrared spectra, it was established that the ratio of 2-methyl-6-isobornylphenol to 2-methyl-4-isobornylphenol in the oily condensation product was 1.9 : 1; this was confirmed also by the data of high frequency titration.

5. With the help of the high frequency titration method, the possibility of a quantitative determination of the isomeric terpene phenols which are differentiated by the position of the terpene substituent in the aromatic nucleus was shown in principle.

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SYNTHESES BASED ON ANABASINE

XIV. SULFONATION OF 4,4'-BIPYRIDINE WITH SULFURIC ACID

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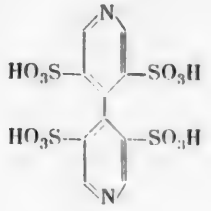
2,3'-Bipyridine-5-sulfonic acid was obtained when the alkaloid anabasine was sulfonated, and a number of its derivatives were prepared [1].

In this paper the results of studying the sulfonation of 4,4'-bipyridine with sulfuric acid are discussed.

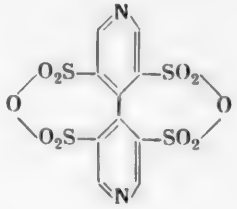
We ran the sulfonation of 4,4'-bipyridine (the same as in the case of anabasine) under the conditions used to sulfonate pyridine [2], i.e., by heating a mixture of 4,4'-bipyridine with a large excess of concentrated sulfuric acid (4 moles of sulfuric acid per mole of 4,4'-bipyridine) for 6 hr at 300-320° (only small amounts of the sulfonic acid were obtained when the 4,4'-bipyridine was sulfonated with sulfuric acid in the ratios 1 : 1, 1 : 2, and 1 : 3). The sulfonic acid obtained was isolated as the barium salt. The potassium and sodium salts were obtained from the latter by exchange reaction.

The free sulfonic acid was obtained by treating the barium salt with an equimolar amount of sulfuric acid. The free sulfonic acid is a crystalline substance, which neither melts nor decomposes when heated to 400°. Determination of the neutralization equivalent and analysis of the barium, potassium and sodium salts indicate that it has the empirical formula $C_{10}H_8N_2(SO_3)_4$ and corresponds to the tetrasulfonic acid of 4,4'-bipyridine.

We assigned the structural formula 4,4'-bipyridine-3,5,3',5'-tetrasulfonic acid (I) to the obtained sulfonic acid.



(I)



(II)

The assumption that the sulfonic groups in the molecule of this acid are found in the β-positions to the nitrogen atoms was made by analogy with the structure of the sulfonic acids of pyridine and 2,3'-bipyridine. Further evidence of this is the difficulty with which the 4,4'-bipyridinesulfonic acid hydrolyzes. Similar to 3-pyridinesulfonic acid, this sulfonic acid does not hydrolyze even when heated in sealed tubes with 25% hydrochloric acid.

To prove the structure of sulfonic acid (I) we ran the following transformations.

The sulfonic acid was dehydrated with P_2O_5, as a result of which we obtained the anhydride of 4,4'-bipyridine-3,5,3',5'-tetrasulfonic acid. The anhydride is basic; it neither melts nor decomposes when heated to 400-450°.

It is possible for the anhydride of 4,4'-bipyridine-3,5,3',5'-tetrasulfonic acid to have the structural formula (II), since it is difficult to depict the formation of the anhydride with any other arrangement of the sulfonic groups in 4,4'-bipyridine.

Proceeding from the fact that 4,4'-bipyridine, despite the apparent equality of the two pyridine rings, is oxidized to isonicotinic acid [3], we subjected sulfonic acid (I) to oxidation. It proved that the oxidation went easier than the oxidation of the starting 4,4'-bipyridine.

Determination of the neutralization equivalent and analysis of the salts of the oxidation product of the 4,4'-bipyridinetetrasulfonic acid indicate that its empirical formula of $C_6H_5O_8NS_2$ corresponds to a disulfoisonicotinic acid. The oxidation product is a white crystalline substance that does not melt when heated to 380-400°, but instead it sublimes.

We proved the structure of the oxidation product by replacing the sulfonic groups by bromine, employing the conditions used to convert 3-pyridinesulfonic acid to 3-bromopyridine [4]. Here we obtained 3,5-dibromoisonicotinic acid with m.p. 62-64°, which in its properties is different from the known 2,6-dibromoisonicotinic acid, having m.p. 184-185° [3].

The formation of the anhydride of 4,4'-bipyridine-3,5,3',5'-tetrasulfonic acid and of 3,5-dibromoisonicotinic acid both support the fact that formula (I) is the most probable for the tetrasulfonic acid of 4,4'-bipyridine. Consequently, its oxidation product is 3,5-disulfoisonicotinic acid.

EXPERIMENTAL

Sulfonation of 4,4'-bipyridine with sulfuric acid. Six milliliters of concentrated sulfuric acid (d 1.84; molar ratio 1 : 4) was added in small portions, with cooling, to 3.9 g of 4,4'-bipyridine. The obtained mixture was heated in a sand bath at 300-320°. The reaction mixture became thick after heating for 6 hr. The reaction product was dissolved in water and then treated with barium carbonate with heating (until neutral or weakly alkaline to litmus). The mixed precipitate of barium sulfate and carbonate was filtered. The filtrate was evaporated to dryness and the residue was digested with alcohol, yielding a crystalline product. The product was filtered and washed with alcohol. We obtained 3.4 g of the barium salt of 4,4'-bipyridinetetrasulfonic acid (yield 20%, based on starting bipyridine). Unreacted 4,4'-bipyridine (about 84%) deposited from the mother liquor on standing.

The barium salt is a white crystalline compound, quite readily soluble in water and insoluble in alcohol and in acetone. For analysis the barium salt was dried in a vacuum oven (1-2 mm) at 100°.

Found %: Ba 35.79, 35.83, 36.19. $C_{10}H_4O_{12}N_2S_4Ba_2$. Calculated %: Ba 36.74.

The potassium salt was obtained by adding an equimolar amount of potassium carbonate to a solution of the barium salt; the filtrate from the separation of the barium carbonate was evaporated. The residue was treated with alcohol. The alcohol solution on standing deposited the potassium salt as a crystalline substance with a pinkish tinge, soluble in water, and insoluble in alcohol.

Found %: K 24.96, 24.82, 24.61. $C_{10}H_4O_{12}N_2S_4K_4$. Calculated %: K 24.79.

The sodium salt was obtained in the same manner as the potassium salt. The salt was recrystallized from hot alcohol. The sodium salt was obtained as a white crystalline substance, readily soluble in water, and difficultly soluble in alcohol. For analysis the salt was dried in a vacuum oven (1-2 mm) at 100°.

Found %: Na 16.5, 16.62, 16.22. $C_{10}H_4O_{12}N_2S_4Na_4$. Calculated %: Na 16.31.

4,4'-Bipyridine-3,5,3',5'-tetrasulfonic acid (I). A solution of 1 g of the Ba salt in hot water was treated with the calculated amount of sulfuric acid. The obtained precipitate of barium sulfate was filtered; the filtrate was evaporated on the water bath to a small volume. The solution on standing deposited white crystals of (I). The sulfonic acid is soluble in boiling water, and is insoluble in alcohol. For analysis the acid was dried in a vacuum oven (1-2 mm) at 100°.

Found: equiv. 118.5, 117.1, 118.0, 117.0. $C_{10}H_8O_{12}N_2S_4$. Calculated %: equiv. 119.0.

Anhydride of 4,4'-bipyridine-3,5,3',5'-tetra sulfonic acid (II). A mixture of (I) (0.5 g) and P_2O_5 was heated in a sand bath at 110-120° for 4 hr. The reaction product was dissolved in a little water, followed by treatment with 40% NaOH solution until strongly alkaline. Then the mixture was evaporated to dryness and the residue was extracted with anhydrous alcohol. The alcohol extract on standing deposited the anhydride (II) as a white crystalline material, which was filtered and dried. Anhydride (II) does not melt when heated to 400-450°.

Found %: S 29.20, 29.18. M 438, 437.5. $C_{10}H_4O_{10}N_2S_4$. Calculated %: S 29.09. M 440.

Oxidation of 4,4'-bipyridine-3,5,3',5'-tetrasulfonic acid (I) was treated with an excess of saturated potassium permanganate solution. The solution was allowed to stand for a day, after which it was heated for 3 hr on the water bath, filtered, and the filtrate was evaporated to dryness. The oxidation product was extracted with anhydrous alcohol, and the alcohol extract was distilled to a small volume.

The residue on standing deposited the crystalline potassium salt of 3,5-disulfoisonicotinic acid.

Found %: K 28.50, 28.23, 28.05. $C_6H_2O_8NS_2K_3$. Calculated %: K 29.30.

3,5-Disulfoisonicotinic acid. The calculated amount of sulfuric acid was added to a water solution of the oxidation product. The mixture was evaporated to dryness and the residue was extracted with anhydrous alcohol. A white substance, subliming at 380-400°, crystallized from the alcohol extract on standing. The substance is acidic in character.

Found: equiv. 93.69, 94.08, 93.76. $C_6H_5O_8NS_2$. Calculated: equiv. 94.33.

3,5-Dibromoisonicotinic acid. The calculated amount of bromine was added in drops to a refluxing solution of 3,5-disulfoisonicotinic acid. Then the reaction product was extracted with ether. Removal of the ether by distillation left a crystalline residue in the flask. Treatment of this residue with acetone gave a pale yellow substance with m.p. 62-64°, exhibiting a weakly acid character. 3,5-Dibromoisonicotinic acid was characterized as the Ba salt.

Found %: Ba 19.21, 19.30; Br 43.66, 43.70. $C_{12}H_4O_4N_2Br_4Ba$. Calculated %: Ba 19.65; Br 45.90.

SUMMARY

1. The sulfonation of 4,4'-bipyridine was studied under the conditions used to sulfonate pyridine. It was established that 4,4'-bipyridine-3,5,3',5'-tetrasulfonic acid is formed here. The sodium, potassium and barium salts of the tetrasulfonic acid were prepared.

2. The dehydration of 4,4'-bipyridine-3,5,3',5'-tetrasulfonic acid gave the corresponding anhydride.

3. The oxidation of 4,4'-bipyridine-3,5,3',5'-tetrasulfonic acid gave 3,5-disulfoisonicotinic acid, which was converted to 3,5-dibromoisonicotinic acid.

4. The obtained compounds are new.

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LETTERS TO THE EDITOR

THE STEREOSELECTIVE COURSE OF THE REACTION BETWEEN CARBETHOXYCARBENE AND THE STEREOISOMERIC 1,2-DIPHENYLETHENES

I. A. D'yakonov, Fu Gui-siya, G. L. Korichev, and M. I. Komendantov

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Original article submitted October 11, 1960

The appearance in the literature of new data [1] in support of the stereoselective character of the reaction of free carbomethoxycarbene with the stereoisomeric 2-butenes [2] caused us to report in this letter the results of our observations on the course of a similar reaction involving carbethoxycarbene and the stereoisomeric 1,2-diphenylethenes.

As the result of reacting 1 mole of trans-stilbene with 1 mole of carbethoxycarbene (obtained by the catalytic decomposition of ethyl diazoacetate in cyclohexane solution at 80°*) we isolated the previously unknown ester (I) (85.3% yield, based on reacted stilbene).

B. p. 136-142° (0.2 mm), n_D^{20} 1.5623, d_4^{20} 1.0927.

Found %: C 80.96; H 6.79. M 267.3. $C_{18}H_{18}O_2$. Calculated %: C 81.18; H 6.84. M 266.2.

The infrared spectrum indicates that (I) contains trans-stilbene (6.12 μ) as impurity. Pure (I), free of the stilbene, was obtained by the hydrolysis of (I) to the acid (II) (see below), followed by the esterification of (II) with alcohol.

B. p. 144.5-145° (0.2 mm), n_D^{20} 1.5631, d_4^{20} 1.0868.

Found %: C 81.08, 81.12; H 6.98, 6.90. $C_{18}H_{18}O_2$. Calculated %: C 81.18; H 6.84.

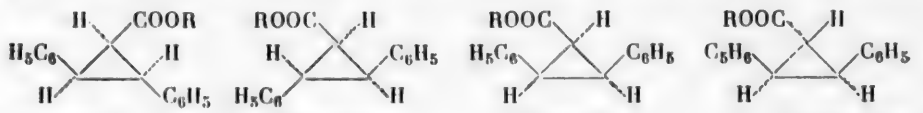
Infrared spectrum, ν in cm^{-1}: 925, 958, 1008, 1034, 1066, 1095, 1176, 1215, 1276, 1356, 1382, 1458, 1512, 1600, 1738.

The alkaline hydrolysis of (I) gave acid (II) in 80% yield.

M.p. 155-157° [4], K_a (in 50% ethanol solution) 0.95×10^{-7}.

Infrared spectrum, ν in cm^{-1}: 950, 1028, 1092, 1156, 1236, 1276, 1332, 1388, 1464, 1700.

Employing d-quinine and *l*-ephedrine, acid (II) was cleaved into the optical antipodes (IIa) and (IIb).**



(Ia) R = C_2H_5; (IIa) R = H; (Ib) R = C_2H_5; (IIb) R = H; (III) R = C_2H_5, (IV) R = H, (IIIa) R = C_2H_5; (IVa) R = H.

* Previously the reaction of ethyl diazoacetate with the stereoisomeric stilbenes was studied under the conditions of heating at 180-200° in the absence of a catalyst [3-5]. In this case the reaction could go with involvement of whole ethyl diazoacetate molecules, rather than of carbethoxycarbene biradicals [3].

** (Ia) + (Ib) = (I); (IIa) + (IIb) = (II).

d-Quinine salt of acid (IIa). M.p. 222-223°. Yield 85%.

Found %: C 76.73, 76.75; H 6.91, 6.81; N 4.97. $C_{36}H_{38}O_4N_2$. Calculated %: C 76.88; H 6.76; N 4.98.

Acid (IIa). M.p. 136-137°. Yield 75% (based on the salt). α_D^{20} + 9.08° (c 0.88, in $CHCl_3$), -23.64° (c 0.23, in C_2H_5OH).

Found %: C 80.88, 80.40; H 5.97, 6.05. $C_{15}H_{14}O_2$. Calculated %: C 80.61; H 5.96.

l-Ephedrine salt of acid (IIb). M.p. 144-145°. Yield 76%.

Found %: C 73.71, 73.61; H 7.59, 7.63; N 3.41. $C_{26}H_{31}O_4N$. Calculated %: C 74.08; H 7.41; N 3.32.

Acid (IIb). M.p. 136-137°. Yield 85% (based on the salt). α_D^{20} -9.08 (c 0.52, in $CHCl_3$) + 23.60° (c 0.23, in C_2H_5OH).

From the fact that acid (II) can be cleaved into its optical antipodes it must be concluded that it has the trans-configuration, and consequently that the cis-addition of carbethoxystilbene to trans-stilbene is stereoselective. The same conclusion was reached as the result of studying the reaction with cis-stilbene (the molar ratio of the reactants and the procedure used to obtain the biradical were the same as in the case of trans-stilbene). The reaction product was the previously unknown ester (III) or (IIIa) (the configuration of the meso form was not established). Yield 63.4%, based on reacted cis-stilbene. M.p. 116-117°.

Found %: C 81.12, 80.91; H 6.90, 6.84. $C_{18}H_{18}O_2$. Calculated %: C 81.18; H 6.84.

Infrared spectrum, ν in cm^{-1}: 1026, 1077, 1190, 1201, 1298, 1388, 1458, 1618, 1720.

As the result of the alkaline hydrolysis (KOH in CH_3OH) of ester (III) or (IIIa) we obtained the corresponding acid as the meso form (IV) or (IVa). M.p. 151-152° [4].

Found: equiv. 235.6, 234.6. $C_{15}H_{13}CO_2H$. Calculated: equiv. 238.3; K_a (in 50% alcohol) 17.1 x 10^{-7}.

Infrared spectrum, ν in cm^{-1}: 950, 1026, 1076, 1103, 1158, 1211, 1288, 1386, 1462, 1492, 1686.

The fact that the acid is not cleaved to the optical antipodes using quinine and ephedrine indicates that it has the cis-(phenylphenyl) configuration and, consequently, that the reaction of the biradical with cis-stilbene is stereoselective. Quinine salt (64% yield), m.p. 185-187° (decomp.).

Found %: C 76.77, 76.66; H 6.64, 6.75; N 4.93, 4.95. $C_{36}H_{38}O_4N_2$. Calculated %: C 76.85; H 6.45; N 4.98.

The reaction of carboethoxycarbene with the cis and trans 4-octenes is also stereoselective. The reaction products are the ethyl esters of the cis and trans d-1,2-diphenyl-3-cyclopropanecarboxylic acids, respectively.

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SYNTHESIS OF TRIALKYLVINYLOXYSILANES FROM ACETYLENE AND SILANOLS

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Original article submitted September 18, 1960

In recent years the silicon-containing vinyl ethers are attracting the attention of chemists in connection with their possible use as monomers for the synthesis of high-molecular compounds. We were the first to synthesize the trialkylvinyloxysilanes and give a general description of their properties [1].

Other authors [2] have shown that it is possible to obtain the trialkylvinyloxysilanes by a different scheme. Attempts by investigators to use the Favorskii–Shostakovskii direct vinylation procedure to synthesize these compounds proved unsuccessful. This gave rise to the premature conclusion that the indicated reaction is not suitable for the preparation of trialkylvinyloxysilanes [3].

A more detailed study by us of the conditions for the direct vinylation of silanols revealed that the main obstacle to the success of this reaction is the great tendency shown by the silanols to convert to disiloxanes under the synthesis conditions. The authors of the present letter proposed using excess acetylene to suppress the undesirable disiloxanization reaction; when this was done it proved possible to obtain the trialkylvinyloxysilanes in accordance with the scheme

$$(R)_3SiOH + nHC{\equiv}CH \longrightarrow (R)_3Si{-}O{-}CH{=}CH_2 + n{-}1HC{\equiv}CH.$$

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POLYCONDENSATION BASED ON THE A. E. ARBUZOV REACTION

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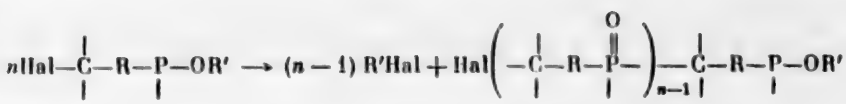
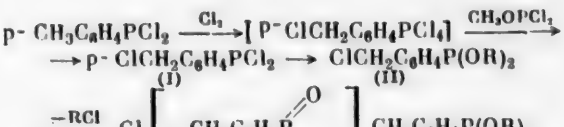
The Arbuzov rearrangement [1] of phosphorous acid esters to pentavalent phosphorus compounds by reaction with halo derivatives can be used to synthesize organophosphorus polymers. For this the phosphorous acid ester and alkyl halide functions should be combined in the monomer molecule, and the polycondensation process can be depicted by the scheme



The first to observe a process of this type was P. A. Rossiiskaya and one of us in the isomerization of tris(2-chloroethyl)phosphite [2]; however, at the time, the polymeric organophosphorus compounds appeared only as secondary products, and their preparation was not the purpose of the investigation.

First we synthesized p-(chloromethyl)phenyldichlorophosphine (I), which served as the starting material in the preparation of the esters of p-(chloromethyl)phenylphosphonous acid (II), which when heated in vacuo at 90-120° form polymers as the result of polycondensation by the Arbuzov rearrangement scheme. The general scheme of the synthesis is:



The treatment of p-tolyldichlorophosphine in chlorobenzene solution with chlorine gave the corresponding tetrachloride, which on further chlorination (UV-light, 80-90°) and subsequent reduction with methoxydichlorophosphine [3] gave p-(chloromethyl)phenyldichlorophosphine (I).

B. p. 98-99° (1 mm), n_D^{20} 1.6127, d_4^{20} 1.4111.

Found %: C 36.8, 36.8; H 2.6, 2.7; P 13.4, 13.4; Cl 47.1, 47.1. $C_7H_6PCl_3$. Calculated %: C 37.0; H 2.7; P 13.6; Cl 46.8.

The reaction of (I) with ethylene oxide gave the di-(2-chloroethyl) ester of p-(chloromethyl)phenylphosphonous acid (II, R = CH_2CH_2Cl).

n_D^{20} 1.5620; d_4^{20} 1.3328.

Found %: C 41.7, 41.8; H 4.4, 4.2; P 9.9, 9.8; Cl 34.0, 33.9. $C_{11}H_{14}O_2PCl_3$. Calculated %: C 41.9; H 4.5; P 9.8; Cl 33.7.

The obtained ester when heated (90-120°, 20 hr) in vacuo gave a clear, glassy, brittle polymer, softening at 15-30°. The molecular weight (determined ebullioscopically in chloroform) was 3250. The polymer is readily soluble in chloroform and alcohol, less readily soluble in benzene and acetone, and is precipitated from the solutions by the addition of petroleum ether; the polymer absorbs moisture from the air. The phosphorus content is 13% and the polymer does not burn. A mixture of polystyrene and the obtained polymer (70 : 30 by weight) forms a mass that softens at 75-85°. It should be mentioned that the mixture ceases to be fire resistant when the amount of the polymer in the mass is around 40%.

The diethyl ester of p-(chloromethyl)phenylphosphonous acid (II, R = C_2H_5) was also converted under similar conditions to a polymeric product.

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STUDIES IN THE FURAN SERIES

XIII. NEW STEREOSPECIFIC SYNTHESIS OF CYCLITOLS

Yu. K. Yur'ev and N. S. Zefirov

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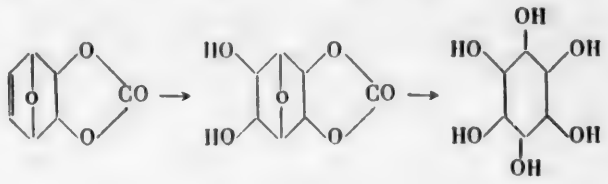
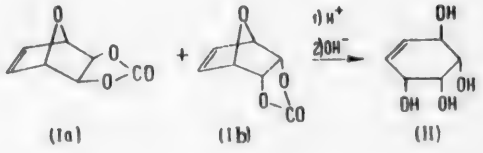
pp. 685-686, February, 1961
Original article submitted October 5, 1960

The synthesis of cyclitols, to which a very large number of papers [1, 2] have been devoted, is still quite tedious at the present time. In addition, many of the methods lead to a resulting mixture of isomeric cyclitols. Continuing our studies on the diene synthesis in the furan series, we decided to study the adduct of furan with vinylene carbonate [3] for the purpose of developing a new synthesis of cyclitols by the scheme of first hydroxylating the double bond in the adduct, followed by opening of the endoxo bridge and subsequent hydrolysis of the carbonate group.



EXPERIMENTAL

A mixture (10 mg) of the exo- and endo-adduct of furan with vinylene carbonate (Ia and b) (m.p. 101-141°; from the literature [3]: m.p. 95-140°) was heated for 1 hr on the boiling water bath with 3 ml of water and 1 drop of 0.1 N sulfuric acid. Then 0.1 g of barium hydroxide was added, the mixture heated for another 4 hr, followed by separation of the precipitate, which was washed well with water, and the filtrate treated with ion-exchange resin KU-2 in the H^+-form and then evaporated in vacuo to dryness. We obtained 4 mg of conduritol C (II): m.p. 150-152° (from anhydrous alcohol) (literature data [4]: m.p. 151-152°).

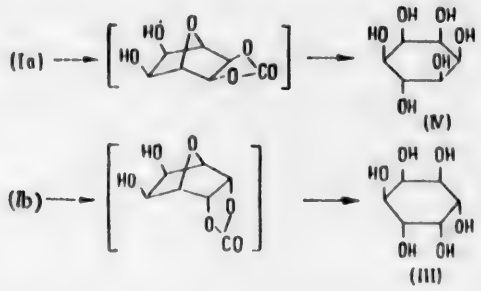


(Ia) (Ib) (II)

Ten milligrams of the mixed adducts was hydrogenated in the presence of 15 mg of $Pd/BaSO_4$, and after the above described treatment (opening of the endoxo bridge and hydrolysis) we obtained 3 mg of dihydroconduritol C as a syrup. Found: R_f 0.66 (phenol–water); 0.38 (butanol–water–acetic acid), which coincides exactly with the R_f given in the literature for dihydroconduritol C in these systems [5].

A solution of 50 mg of the mixed adducts in 3 ml of ethanol was hydroxylated with 1% potassium permanganate solution in the presence of magnesium sulfate by the method of [1], after which the mixture was filtered, the precipitate washed with water and alcohol, the filtrate evaporated to dryness, and the residue dissolved in 5 ml of water and then treated with 0.1 N sulfuric acid solution in drops until acid; then the solution was heated for 2 hr. 0.2 g of barium hydroxide was added, the mixture heated on the water bath for 5 hr, filtered, the precipitate washed with water, and the filtrate treated with ion-exchange resin KU-2 in the H^+-form. Evaporation of the solution gave 10 mg of syrup, which crystallized on standing. Recrystallization from anhydrous alcohol gave 4 mg of neoinositol (III), which melts at 313° (with decomp.). Literature data [1]: m.p. 315° (with decomp.).

It was established by paper chromatography that, besides neo-inositol and other substances, the syrup also contains epi-inositol (IV): R_f 0.37 (phenol–water); 0.11 (butanol–water–acetic acid), which coincides with the literature data for the R_f of epi-inositol in these systems [5].



It is obvious that using the pure exo- and endo-adducts leads to obtaining the pure inositol. Such a synthesis of the hexitols is stereospecific, for cis-hydroxylation should be by exo-addition. Work in this direction is being continued.

The publication of these preliminary results of our work was prompted by the recent letter of Sarel and Kowarsky [6] to the Editor, in which the possibility of synthesizing hexitols by such a scheme and obtaining allo- and meso-inositols was indicated.

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CONCERNING THE PAPER BY M. BATUEV ON "THE PROBLEM OF CONJUGATION IN BENZENE"

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The paper by M. Batuev [1], composed as an empirical compilation of various measurement data lying outside the physical meaning of the phenomena, disorientates the chemist. For this reason I consider it necessary to bring to the attention of chemists the physical meaning of the experimental data compiled by M. Batuev.

1. The metal-like character of the benzene ring is a physical phenomenon. Like any physical phenomenon, it is studied with an accuracy approaching the actual fluctuations of the values of the characteristic quantities. The consecutive measuring of the same characteristic quantity has a tendency to group the values around some average (for the given sequence) value. As the number of measurements increases, the average value for the given sequence conjecturally reduces the limiting average value. The individual measurement values differ from the limiting average because of uncontrollable or change fluctuations in the external conditions or in the measurement technique. Increasing the accuracy of the measurements enables recording of the fluctuations precisely. These individual values follow some distribution around the limiting average. The details of this distribution are expressed as a mathematical distribution law, depending on several parameters (limiting average, degree of scattering of the values, etc.). The experimenter has at his disposal only the final collection of chance measurements, which is only a part of the possible infinite sequence of the measurements. Estimating functions can give either a direct approximate value of the characteristic quantity, or they can indicate the practical trustworthy limits, within which the values of this quantity lie. Also, the same as one method of measuring can have an advantage over another method, one method of finding the estimate (use of an estimating function) can have an advantage over other methods. The true function, determining the statistical distribution of the direct measurements, cannot be established exactly. For this reason the validity of the conclusions, derived from the experimental data, depends on the success with which the form of the distribution was selected. Any hypothesis, based on the final collection of the data of consecutive measurements, should be subjected to statistical verification. The theory of phenomena is not created on the elementary values of characteristic quantities, but on the characteristic multitudes of the values of these quantities. Fluctuations give a statistical character to the theory of phenomena.

The metal model of the benzene ring does not postulate a rigidly geometric hexagonal structure for the benzene ring. Practical organic chemistry manipulates statistical multitudes of molecules. Theoretical organic chemistry strives to understand, describe, and model a single molecule. A unity of the statistical character of measurements and the individuality of the model of the molecule is achieved when knowing the physical meaning of phenomena. Under the conditions of our planet—under the kinetic and electron-ionic bombardments in the mass of the substance, in the force fields, and in the streams of radiant energy—the molecule cannot be a geometrically regular system. The factors of the capacity and intensity of the characteristic value of each bond in the benzene ring are subject to fluctuations. A momentary difference between the bonds is possible at any given moment, i.e., a momentary disturbance of the hexagonal symmetry D_6h of the benzene ring. The limiting average value of the characteristic quantity, around which the fluctuations are grouped, is the same for all of the bonds; the limiting average value for the symmetry of the benzene ring is D_6h.

M. Batuev collected the details of the statistical distribution of separate direct measurement values—values of the fluctuations, chance values of the characteristic quantities—and assigned them an absolute value, rather than a statistical value, as would follow from a conformity of the metal-like nature of the benzene ring with the physical meaning of phenomena.

TABLE 1 [3-9].

Bond	Characteristic				
	l (in A)	Q (in kcal/mole)	ν (in cm^{-1})	$\alpha \cdot 10^{25}$	
				∥	⊥
$C_{al.}-C_{al.}$	1.50—1.60	58—71	1000	18.8	0.2
$CC_{ar.}$	1.39—1.45	96	1585	22.5	4.8
$C_{al.}=C_{al.}$	1.30—1.35	111—134	1670	28.6	10.6
$C_{al.}\equiv C_{al.}$	1.20	166	2220	35.4	12.7

The statistical table (Table 1) indicates the practical trustworthy limits, within which lie the values of the quantities, characteristic for the bonds between carbon atoms (the symbols are generally accepted).

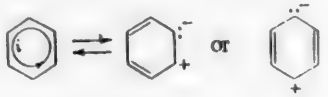
The bonds in the benzene ring are quite different from the bonds that are possible between other types of carbon atoms. As the unsaturation of the bond between carbon atoms increases, the covalent grouping of the electrons approaches that of an octet. The bond becomes stabilized, and the amplitude of the fluctuations of the characteristic quantities decreases; the dispersion spectrum of the chance fluctuations diminishes [2].

TABLE 2 [3, 18].

Direction	Characteristic		
	$\varkappa \cdot 10^{6}$	$\alpha \cdot 10^{25}$	log ε
∥	—37	123.1	3.0
⊥	—91	63.5	2.4

On increasing the accuracy of the measurements the deforming action of the measuring agent, especially electronic and hard x-rays, also becomes actual. For example, determination of the interatomic distances by the Raman spectra method is 5-20 times more accurate than determination by electron-diffraction method [10]. Consequently, in employing an estimating function it is also necessary to take into account the principle of uncertainty. For the covalent electrons of the bonds in the benzene ring the ratio of the uncertainties of the space wave package $\underline{x}$ and the wave number $\underline{\nu}'$ is actual. Within the limits of the fluctuations, $\Delta x \cdot \Delta \nu' \geqslant 1$. The oscillation period of the electron wave is of the same order as that of the light wave, i.e., 10^{-15}. Measuring the time with this accuracy, $\Delta E \cdot \Delta t \geqslant h$, causes an uncertainty in the energy exceeding 1 ev. Consecutive measurements, determining the parameters of the light particles (σ and π-electrons), give a "smeared" picture; the massive particles (carbon nuclei) behave "classically."

2. The dipole moment of a molecule in solution is calculated using the Debye equation, which was derived on the assumption that reaction between the molecules is absent. The partial molar volumes of the solvent and dissolved substance are taken to be independent of the mole fraction [10]. Increasing the accuracy of the measurements permits detection of polarizing effect of intermolecular reaction. The mechanism of this polarizing effect is variable: coordination, dipole, dispersion, hydrogen bond. The benzene ring is sensitive to the influence of the medium (solvent and force fields). Intermolecular reaction induces an elastic ortho- or para-dipole in the benzene ring:



Polarization of the benzene ring is proportional to the intensity of the intermolecular reaction. Especially strong polarization of the benzene ring occurs in polar solvents. In nitrobenzene solution ($\mu C_6H_5NO_2$ = 3.93 D), for example, the induced dipole moment of benzene reaches 1.2 D [11]. Holland and Le Fevre apply the term "apparent" to the dipole moment induced by the solvent [11]. The induced polarization of the benzene ring is reversible [12]. The factor of the "apparent" polarity of benzene lies outside the benzene ring.

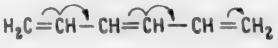
TABLE 3 [21, 26].

Molecule	Characteristic		
	K	$\mu \cdot 10^{18}$	Q (in kcal)
	+ 3.0	0	—
	+ 7.2	0.61	+28.6
	+10.7	1.2	+26.8
	— 1.4	0	— 5.6

K is the constitutive component of the diamagnetic susceptibility: $\chi_{mol.} = \Sigma\chi_{at} + k$;
Q is the energy for the addition of 1 hydrogen molecule.

3. The constancy of the magnitude in the compression of the molecular volume in the series cyclohexane–cyclohexene–cyclohexadiene–cyclohexatriene (benzene) is trivial, for the reason that the capacity factor for each double bond entering the ring at the moment of formation is constant. This factor does not relate to the further fate of the double bond entering the ring and cannot be its criterion.

4. The similarity in the light absorption of cyclohexatriene (benzene) and hexatriene testifies to the closeness in the energies of their electron systems, which is characteristic for the conjugation of three double bonds. In the hexatriene molecule the conjugation is expressed in unilateral ebbs and flows of the π-electrons,



while in the cyclohexatriene (benzene) molecule a continuous path of the π-electron wave is opened, forming a closed current of superconductivity with the resulting magnetic flux [13].

Some difference in the light absorption is due to cyclization. The electrons in the benzene ring are delocalized due to conjugation of the three double bonds from the moment of their formation. The π-electron current established along the perimeter of the benzene ring tends to equalize its electron density. When the molecular system of benzene is in the state of a closed superconductor the gain in energy is 5.6481×10^{-13} erg when compared with the cyclohexatriene state [13].

5. The stationary π-electron current along the perimeter of the benzene ring is described by the Maxwell equations: rot E = 0, j = rot H. From the second equation it follows that divj = 0, where j is the current density of the conductance. This means that the electricity in the benzene superconductor behaves like an incompressible liquid. The π-electron current becomes stronger or weaker with fluctuation contraction or expansion of the benzene superconductor. The conservation theorem is formulated on the basis of the analogy between the conductor of the π-electron current and a vortex tube:

$$\frac{d}{dt}(\omega d\sigma) = 0,$$

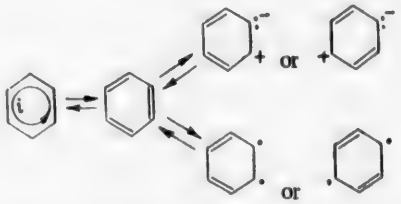
where ω is the angular velocity, and $d\sigma$ is the element of the surface. Since divrot = 0, then $\operatorname{div}\omega = 0$. The angular velocity flow through each element of the surface, moving with π-electron current of the benzene ring, retains a constant value [14, 15]. The fluctuations of the benzene contour attract a pulsation of the π-electron current in it, but they do not stop it, the same as the orbital ampere currents do not cease in the deformed chemical bond of the atom. Increasing the ring of conjugated multiple bonds eliminates the coplanarity contour. The cyclooctatetraene and chlorophyll molecules are distorted [16, 17]. In the distorted contour, due to variation of the current in the area, self-induction operates. The induced emf excites a damping extra current, which prevents superconductivity. The statistics of the equiprobable orientation of the ampere currents of the benzene rings and mutally compensating resultant magnetic fluxes explain the diamagnetism of benzene.

The closed current of the superconductivity of the benzene ring is equivalent to the magnetic dipole and is characterized by the anisotropy of the diamagnetic susceptibility χ. Of the 42 electrons in the benzene molecule only 6 exert a strongly anomalous influence on the anisotropy of the diamagnetic susceptibility. Due to the fluc-

tuations of the benzene ring, momentary disturbances of the isotropy in its plane are possible. The axial symmetry of the distribution of the π-electron density in the benzene ring D_{6h} determines the anisotropy of the polarizability α and light absorption (dichroism) ϵ. Statistical Table 2 indicates the practical trustworthy values of the quantities, characteristic for the anisotropy of the benzene ring.

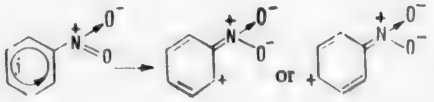
Diamagnetic anisotropy is inherent in any molecule that has a symmetrical distribution of the electron density different from spherical. Disturbances of the spherical symmetry vary: in the benzene molecule—due to its metal-like nature; in an aliphatic molecule with a covalent double bond—due to arrangement of the atoms in a plane perpendicular to it; in addition, conjugation with the multiple bond deflects some of its coplanar electron orbits [19].

6. Chemical reaction is characterized by energy values ranging from 0.1 to 10 ev, i.e., from 1.6018×10^{-13} to 1.6018×10^{-11} erg; the photochemical effect of light quanta is characterized by energy values ranging from 1.2 to 12 ev, i.e., from 0.1922×10^{-11} to 1.9222×10^{-11} erg [20, 21]. The energy of the closed π-electron current in the benzene contour is estimated at 5.6481×10^{-13} erg [13]. If the energy of the chemical action of benzene exceeds the electromagnetic energy of the benzene ring, there occurs an opening of the π-electron current, a localization of the double bonds and their polarization or radicalization depending on the state of the reagent and the dielectric permeability of the medium. Photochemical action on benzene disturbs its metal-like nature unconditionally. Chemical and photochemical reactions of benzene are initiated with a polarization or radicalization of the benzene ring.

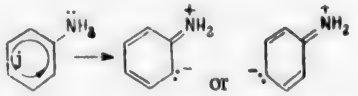


The apparent unsaturation of benzene in reactions of ozonization, photochemical halogenation and catalytic hydrogenation is determined by energy factors. The rate of fluctuations of the σ, π-electron and nuclear systems of the benzene ring is, respectively, 15 and 12 orders of magnitude greater than the rate of the chemical reactions of benzene. According to the Franck—Condon principle, the deformation fluctuations of the benzene ring are not actual for the chemical properties of benzene. The chemical properties of benzene depend on the limiting average values of the quantities, characteristic for the benzene ring: bond length, dipole moment, polarizability, diamagnetic susceptibility, etc.

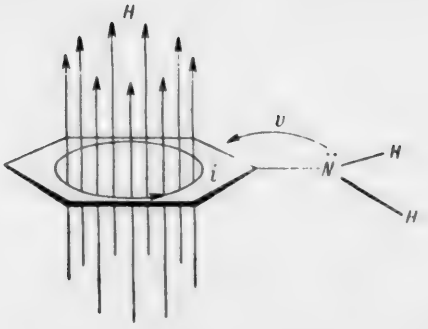
7. The benzene ring is sensitive to the influences of substituents. Electron-acceptor functional groups ($-NO_2$, $-SO_2OH$, $-COOH$) decrease the current density of the conductivity $\underline{j}$ of the benzene contour, for example



This leads to a rupture of the continuity of the current density $\underline{j}$. The condition of closure of the current lines is violated, and the benzene contour ceases to satisfy the continuity equation $\mathrm{div}\, j = 0$ [22]. Electron-donor functional groups ($-\ddot{N}H_2$, $-\ddot{O}H$, $-\ddot{C}l:$) increase the current density of the conductivity $\underline{j}$ of the benzene contour, for example



The resultant magnetic field of the closed π-electron current in the benzene contour deflects by Lorentz force [23] the noncovalent electrons of the donor atom (N, O, Cl) in the ring (Figure). The Lorentz force is perpendicular to the direction



of motion of the electrons $\bar{v}$ and to the direction of the magnetic field H. This force only bends the path of the electron, not changing the numerical value of its velocity, i.e., not doing any mechanical work. In the steady homogeneous magnetic field of the benzene ring the electrons of the amino group (hydroxyl group, chlorine) strive to describe a spiral line, the axis of which coincides with the direction of the field. Since the initial velocity of the electrons in the donor atom is perpendicular to the direction of the magnetic field H, then the spiral trajectory degenerates in the periphery. There occurs a precession of the noncovalent electrons around the direction of the magnetic field H. The radius of the periphery, described by the electrons is calculated using the equation: $r = \frac{c \cdot m \cdot \bar{v}}{e \cdot H} \cdot \sin(\bar{v}H)$ [23]; $\bar{v} = e \cdot \sqrt{\frac{Z}{m \cdot r_{N,\,O,\,Cl}}}$, H = 31.0204 · 10^4 oersteds [13]; r_N 0.7, r_O = 0.66 A, r_{Cl} = 0.99 A, e = 4.806 · 10^{-10} CGSE, c = 2.9977 · 10^{-10} cm/sec; m = 9.106 · 10^{-28} g [22].

In hydrogen compounds the distances between the nuclei are not additive to the radii of the atoms. The bond of hydrogen with another element is always shorter than its ionic radius. The proton penetrates into the electron sphere of the nitrogen (oxygen) atom by 1/4 or 1/3 (or deeper) of its effective radius. The penetration of the proton is limited by the coulomb repulsion of the ring [24]. The central charge on the amino group is created by the nucleus of the donor nitrogen atom and two protons: $Z_{NH_2} = Z_N + Z_{2H^+} = 7 + 2 = 9$ CGSE. The rate of movement of the electrons is $\bar{v}_N = 5.710 \cdot 10^{-4}$ cm. Comparison with the radius of the benzene contour (1.2037 · 10^{-8} [13]), closing the π-electron current, shows a difference of four orders of magnitude: $\frac{1.038 \cdot 10^{-4}}{1.2037 \cdot 10^{-8}} = 0.854 \cdot 10^4$

The central charge on the hydroxyl group is created by the nucleus of the oxygen donor atom and one proton: $Z_{OH} = Z_O + Z_{H^+} = 8 + 1 = 9$ CGSE. The rate of movement of the electrons is $\bar{v}_O = 5.875 \cdot 10^8$ cm/sec. The precession redius of the noncovalent electrons is r = 1.076 · 10^{-4} cm. Comparison with the radius of the benzene contour, closing the π-electron current, shows a difference of four orders of magnitude: $\frac{1.076 \cdot 10^{-4}}{1.2037 \cdot 10^{-8}} = 0.893 \cdot 10^4$.

The central charge on the donor chlorine atom is created by its nucleus: $Z_{Cl} = 17$ CGSE. The rate of movement of the electrons is $\bar{v}_{Cl} = 6.598 \cdot 10^8$ cm/sec. The precession radius of the noncovalent electrons is r = 1.215 · · 10^{-4} cm. Comparison with the radius of the benzene contour, closing the π-electron current, shows a difference of four orders of magnitude: $\frac{1.215 \cdot 10^{-4}}{1.2037 \cdot 10^{-8}} = 1.009 \cdot 10^4$.

The precession radius of the noncovalent electrons is 10,000 times greater than the radius of the benzene contour. When compared to the radius of the benzene contour, the precession radius is infinitely large. The curvature of the precession is 10,000 times smaller than the curvature of the benzene contour. Under the influence of the Lorentz force the periphery, along which the π-electron current of the superconductivity in the benzene ring is closed, degenerates into a straight line. This means an opening of the condensed current of the superconductivity and a momentary localization of the precessing pairs of noncovalent electrons in the ortho- and para-positions. In the vibrational spectra of benzene the bands of the double bonds are absent; in the vibrational spectra of benzene derivatives the bands of the double bonds are present [25]. The conditions for localization of the electrons in the benzene ring under the influence of the amino and hydroxyl functional groups are the same. This explains the chemical similarity of aniline and phenol in reactions involving the benzene ring.

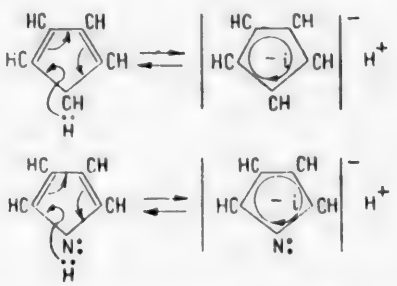
8. Contrary to formal unsaturation, empirically expressed as C_nH_{2n-6}, the cyclohexatriene state is unnatural for benzene. The benzene ring is a substrate for the inversion of multiple bonds. The benzene ring is a characteristic functional grouping for aromatic compounds. The term "aromaticity" should be understood to mean the ability to participate in substitution reactions contrary to formal unsaturation. The aromaticity of benzene is the chemical manifestation of closure of the π-electron current in the benzene contour. Statistical Table 3 indicates the practical trustworthy values of the quantities elucidating the characteristic nature of the benzene ring.

The π-electron current of the superconductivity represents the limiting, higher, form of π-conjugation. The benzene ring is the most economical form of π-conjugation. Its 6 carbon atoms, practically speaking, are held together by a smaller number of electrons than in the hexatriene molecule. The superconductivity electrons are delocalized. The ring of 6 nuclear power centers functions as a reservoir for them. Reacting with other functional groups, the benzene ring withstands both the influx and the loss of electrons. Its electron capacity is reciprocal. The benzene electron reservoir is plastic; functional groups impose their energetic imprint on the benzene ring, shaping its electron system.

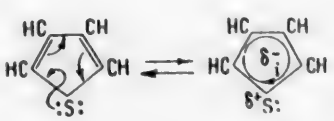
The typical peculiarities of the carbon atom are inherent in the benzene ring: coulomb indifference, ability to combine with both electron donors and electron acceptors, stability. The benzene ring is a natural result of the evolution of the carbon atom, the peculiarities of which are expressed by the middle position of the group IV elements in the periodic system. For aromatic compounds,the benzene ring is just as elemental as the carbon atom is for aliphatic compounds.

The energetic plasticity endows the benzene ring with buffer properties, protecting the molecule from either a sharp influx or a sharp loss of electrons. The benzene ring is the stabilizer of the electron system of the molecule. It serves as an electron reservoir, making up the discharge and absorbing the influx of electrons. Aromatic compounds are much more stable toward the action of high energy (1-9 mev) radiations (α, n, p, $\beta^{\pm}$) than the alkanes; alkenes and polyenes prove to be intermediate in this respect [20]. Benzene is exceedingly stable toward radiolysis, especially in the liquid state. Due to the abundance of energy levels, the benzene ring is a powerful acceptor of excess energy, protecting even substances dissolved in benzene from radiolysis [21]. The aromatic hydrocarbons have especially high octane numbers (98-100) [27]. As a factor for preservation of the molecule the benzene ring is one of the most important products of the chemical evolution of matter. A perfection of π-conjugation, the first manifestation of which is the aliphatic system of conjugated multiple bonds (polyenic), was achieved in the benzene ring. The preservation of living matter is determined by the reversibility of the reactions of molecular systems with the medium. The guarantee of reversibility is π-conjugation in general, and the benzene ring in particular. In the very fine regulators of life processes taking place in protein material (hormones, ferments, vitamins), the benzene ring and the aliphatic system of conjugated multiple bonds are coupled. Live substance could be composed only as a complex of protein base and benzenoid regulator. The metal model of the benzene ring hides the possibility of piercing into the important problems of natural science.

9. The metal model explains the aromaticity of the pentadiene and pyrrole anions.



The metal explains the aromaticity of the thiophene molecule and the non-oxidizability of the sulfur atom in it.



The molecules of many other nonbenzenoid aromatic compounds have a metal-like character [28]. A metal-like character is also inherent to the protein micelle, where a transfer of electrons via a system of hydrogen bonds and peptide groupings takes place, and it also inherent to polymer molecules [29].

Incorrect understanding and the used final collection of haphazard measurements should not be contrasted against the vast and profound physical meaning of the phenomena of metal similarity. Contrasting the statistical character of the measurements and the individuality of the model of the molecule prevents knowing the physical meaning of the phenomena of the metal-like nature of the benzene ring. Rejection of the mesomeric-resonance theory and defense of the position of A. M. Butlerov does not excuse the erroneous nature of M. Batuev's conclusions.

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THE STRUCTURE OF THE ALKALOID DUBINIDINE

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Translated from Zhurnal Obshchei Khimii, Vol. 31, No. 2,
pp. 693-694, February, 1961
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Recently a paper was published in which a study was made of the alkaloid dubinidine, isolated from certain species of Haplophyllum [1]. In this paper the authors propose structure (I) for dubinidine on the basis of the following experimental results obtained by them:

1) the rigorous oxidation of dubinidine gave the known 2-hydroxy-4-methoxy-3-quinolinecarboxylic acid (dictamnic acid);

2) 1 mole of periodic acid was consumed in the oxidation of 1 mole of the alkaloid;

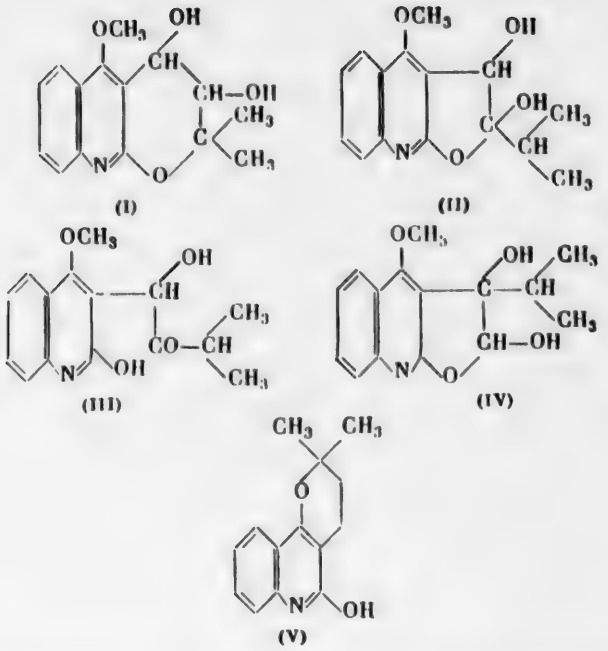
3) the careful oxidation of the alkaloid with potassium permanganate in acid medium gave isobutyric acid.

We will now examine how the data given in the paper agree with the formula (I) proposed by the authors. The obtaining of dictamnic acid indicates that the alkaloid is a derivative of γ-methoxyquinoline and that the oxidized portion of the alkaloid molecule is attached to the pyridine ring, i.e., the benzene ring of the quinoline nucleus is unsubstituted. It is obvious that this is in good agreement with formula (I). This formula also does not contradict the results from oxidizing the alkaloid with periodic acid, showing that it is possible to have the two hydroxyl groups attached to adjacent carbon atoms. However, here it should be emphasized that on the basis of the experimental data given in the paper, i.e., when based only on the amount of consumed periodic acid, without making a study of the oxidation products, it is only possible to suggest such a possibility and in no case can it be said that this is actually so. Other structural elements are also known, for example, α-ketols, α-diketones, etc., that behave like 1,2-glycols when oxidized with periodic acid. Finally, the formation of isobutyric acid when dubinidine is oxidized with potassium permanganate can in no way be explained if one starts with the structure expressed by formula (I). Actually, to form isobutyric acid under these conditions it is necessary to have an unoxidized isopropyl group present, which is absent in formula (I). The assumption that its formation is possible as the result of reducing the carbon atom attached to the two methyl groups is improbable in an oxidizing medium. As a result, dubinidine cannot have the structure (I) proposed for it by the above mentioned investigators.

I believe that a much more probable structure for dubinidine is that expressed by formula (II). This formula fully explains the above given experimental data of the authors, including the formation of isobutyric acid. According to this formula, dubinidine should be classified with the numerous group of furanoquinoline alkaloids, and it can be regarded as being a cyclic polyketal of the ketone with structure (III). Such a structure for alkaloids is not new: as is known, isofebrifugine [2] is assigned an analogous cyclic polyketal structure.

It is easy to see that the experimental data given in the indicated paper are in good agreement with both formulas (II) and (III), and to choose between them at the present time, on the basis of only the above data, is impossible. For the final choice it is necessary to have conclusive proof of the absence (or presence) of a carbonyl group in the alkaloid molecule and, what is especially important, it is necessary to make a study of the infrared spectrum of the molecule.

On the basis of the experimental data given in the paper it is also possible for dubinidine to have either structure (IV) or the structure of the aldehyde corresponding to this cyclic polyacetal. However, when these structures are compared with the closely analogous structures of flindersine [3], lunacridine and hydroxylunacridine [4], having an isoamyl chain of carbon atoms in the β-position of the quinoline nucleus, then for dubinidine, by analogy with these alkaloids, preference should be given to either formula (II) or (III).



As regards the similarity mentioned in the paper between the UV-spectra of dubinidine and dihydroflindersine, the latter being a pyranoquinoline derivative (which, in all probability, caused the authors of the paper to erroneously assign structure (I) to dubinidine), then this similarity cannot have great importance: When all of the five structures depicted above, of which (V) is the formula for dihydroflindersine [3], are compared, it is easy to see that they all differ among themselves by such structural elements as are incapable of strongly affecting their UV-spectra.

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All abbreviations of periodicals in the above bibliography are letter-by-letter transliterations of the abbreviations as given in the original Russian journal. *Some or all of this periodical literature may well be available in English translation.* A complete list of the cover-to-cover English translations appears at the back of this issue.

Soviet Journals Available in Cover-to-Cover Translation

ABBREVIATION	RUSSIAN TITLE		TITLE OF TRANSLATION	PUBLISHER	TRANSLATION BEGAN Vol.	Issue	Year
AÉ	Atomnaya énergiya		Soviet Journal of Atomic Energy	Consultants Bureau	1	1	1956
Akust. zh.	Akusticheskii zhurnal		Soviet Physics – Acoustics	American Institute of Physics	1	1	1955
	Antibiotiki		Antibiotics	Consultants Bureau	4	1	1959
Astr(on). zh(urn).	Astronomicheskii zhurnal		Soviet Astronomy–AJ	American Institute of Physics	34	1	1957
Avto(mat). svarka	Avtomaticheskaya svarka		Automatic Welding	British Welding Research Association (London)		1	1959
	Avtomatika i Telemekhanika		Automation and Remote Control	Instrument Society of America	27	1	1956
	Biofizika		Biophysics	National Institutes of Health*		1	1957
	Biokhimiya		Biochemistry	Consultants Bureau	21	1	1956
Byull. éksp(erim). biol. i med.	Byulleten' éksperimental'noi biologii i meditsiny		Bulletin of Experimental Biology and Medicine	Consultants Bureau	41	1	1959
DAN (SSSR) / Dokl(ady) AN SSSR	Doklady Akademii Nauk SSSR		The translation of this journal is published in sections, as follows:				
			Doklady Biochemistry Section	American Institute of Biological Sciences	106	1	1956
		Life Sciences	Doklady Biological Sciences Sections (Includes: Anatomy, biophysics, cytology, ecology, embryology, endocrinology, evolutionary morphology, genetics, histology, hydrobiology microbiology, morphology, parasitology, physiology, zoology sections)	American Institute of Biological Sciences	112	1	1957
		Life Sciences	Doklady Botanical Sciences Sections (Includes: Botany, phytopathology, plant anatomy, plant ecology, plant embryology, plant physiology, plant morphology sections)	American Institute of Biological Sciences	112	1	1957
		Chemical Sciences	Proceedings of the Academy of Sciences of the USSR, Section: Chemical Technology	Consultants Bureau	106	1	1956
		Chemical Sciences	Proceedings of the Academy of Sciences of the USSR, Section: Chemistry	Consultants Bureau	106	1	1956
		Chemical Sciences	Proceedings of the Academy of Sciences of the USSR, Section: Physical Chemistry	Consultants Bureau	112	1	1957
		Earth Sciences	Doklady Earth Sciences Sections (Includes: Geochemistry, geology, geophysics, hydrogeology, mineralogy, paleontology, petrography, permafrost sections)	American Geological Institute	124	1	1959
		Earth Sciences	Proceedings of the Academy of Sciences of the USSR, Section: Geochemistry	Consultants Bureau	106-123	1-6	1957-1958
		Earth Sciences	Proceedings of the Academy of Sciences of the USSR, Sections: Geology	Consultants Bureau	106-123	1-6	1957-1958
		Mathematics	Doklady Soviet Mathematics	The American Mathematics Society	131	1	1961
		Physics	Soviet Physics–Doklady (Includes: Aerodynamics, astronomy, crystallography, cybernetics and control theory, electrical engineering, energetics, fluid mechanics, heat engineering, hydraulics, mathematical physics, mechanics, physics, technical physics, theory of elasticity sections)	American Institute of Physics	106	1	1956
		Physics	Proceedings of the Academy of Sciences of the USSR, Applied Physics Sections (does not include mathematical physics or physics sections)	Consultants Bureau	106-117	1	1956-1957
Derevoobrabat. prom-st'.	Derevoobrabatyvayushchaya promyshlennost'		Wood Processing Industry	Timber Development Association (London)		9	1959
	Élecktrosvyaz		Telecommunications	Massachusetts Institute of Technology*		1	1957
Éntom(ol). oboz(renie)	Éntomologicheskoe obozrenie		Entomological Review	American Institute of Biological Sciences	38	1	1959
Farmakol. (i) toksikol(ogiya)	Farmakologiya i toksikologiya		Pharmacology and Toxicology	Consultants Bureau	20	1	1957
FMM	Fizika metallov i metallovedenie		Physics of Metals and Metallography	Acta Metallurgica*	5	1	1957
Fiziol. zhurn. SSSR (im. Sechenova)	Fiziologicheskii zhurnal im. I. M. Sechenova		Sechenov Physiological Journal USSR	National Institutes of Health*		1	1957
Fiziol(ogiya) rast.	Fiziologiya rastenii		Plant Physiology	American Institute of Biological Sciences	4	1	1957
	Geokhimiya		Geochemistry	The Geochemical Society		1	1958
FTT	Fizika tverdogo tela		Soviet Physics–Solid State	American Institute of Physics	1	1	1959
Izmerit. tekh(nika)	Izmeritel'naya tekhnika		Measurement Techniques	Instrument Society of America		1	1959
Izv. AN SSSR, O(td). Kh(im). N(auk)	Izvestiya Akademii Nauk SSSR: Otdelenie khimicheskikh nauk		Bulletin of the Academy of Sciences of the USSR: Division of Chemical Sciences	Consultants Bureau		1	1952

continued

Izv. AN SSSR, O(td). T(ekhn). N(auk): Met(all). i top.	(see Met. i top.)					
Izv. AN SSSR Ser. fiz(ich).	Izvestiya Akademii Nauk SSSR: Seriya fizicheskaya	Bulletin of the Academy of Sciences of the USSR: Physical Series	Columbia Technical Translations		1	1954
Izv. AN SSSR Ser. geofiz.	Izvestiya Akademii Nauk SSSR: Seriya geofizicheskaya	Bulletin (Izvestiya) of the Academy of Sciences USSR: Geophysics Series	American Geophysical Union		1	1954
Izv. AN SSSR Ser. geol.	Izvestiya Akademii Nauk SSSR: Seriya geologicheskaya	Izvestiya of the Academy of Sciences of the USSR: Geologic Series	American Geological Institute		1	1958
Kauch. i rez.	Kauchuk i rezina	Soviet Rubber Technology	Research Association of British Rubber Manufacturers	18	1	1959
	Kinetika i kataliz	Kinetics and Catalysis	Consultants Bureau	1	3	1960
	Koks i khimiya	Coke and Chemistry USSR	Coal Tar Research Association (Leeds, England)		1	1958
Kolloidn. zh(urn).	Kolloidnyi zhurnal	Colloid Journal	Consultants Bureau	14	1	1952
	Kristallografiya	Soviet Physics – Crystallography	American Institute of Physics	2	1	1957
Metalov. i term. obrabot. metal.	Metallovedenie i termicheskaya obrabotka metallov	Metal Science and Heat Treatment of Metals	Acta Metallurgica	6	1	1958
	Metallurg	Metallurgist	Acta Metallurgica		1	1957
Met. i top.	Metallurgiya i topliva	Russian Metallurgy and Fuels	Eagle Technical Publications		1	1960
Mikrobiol.	Mikrobiologiya	Microbiology	American Institute of Biological Sciences	26	1	1957
OS	Optika i spektroskopiya	Optics and Spectroscopy	American Institute of Physics		6	1959
	Pochvovedenie	Soviet Soil Science	American Institute of Biological Sciences		1	1958
	Priborostroenie	Instrument Construction	British Scientific Instrument Research Association		1	1959
Pribory i tekhn. éks(perimenta)	Pribory i tekhnika éksperimenta	Instruments and Experimental Techniques	Instrument Society of America		1	1957
Prikl. matem. i mekh.	Prikladnaya matematika i mekhanika	Applied Mathematics and Mechanics	American Society of Mechanical Engineers		1	1958
PTÉ	(see Pribory i tekhn. éks.)					
	Problemy Severa	Problems of the North	National Research Council of Canada			
Radiotekh.	Radiotekhnika	Radio Engineering	Massachusetts Institute of Technology*	12	1	1957
Radiotekh. i élektronika	Radiotekhnika i élektronika	Radio Engineering and Electronics	Massachusetts Institute of Technology*	2	1	1957
	Stanki i instrument	Machines and Tooling	Production Engineering Research Assoc.		1	1959
	Stal'	Stal (in English)	Iron and Steel Institute		1	1959
Stek. i keram.	Steklo i keramika	Glass and Ceramics	Consultants Bureau	13	1	1956
Svaroch. proiz-vo	Svarochnoe proizvodstvo	Welding Production	British Welding Research Association		4	1959
Teor. veroyat. i prim.	Teoriya veroyatnostei i ee primenenie	Theory of Probability and Its Applications	Society for Industrial and Applied Mathematics		1	1956
Tsvet. Metally	Tsvetnye metally	Nonferrous Metals	Primary Sources		1	1960
UFN	Uspekhi fizicheskikh Nauk	Soviet Physics – Uspekhi (partial translation)	American Institute of Physics	66	1	1958
UKh	Uspekhi khimii	Russian Chemical Reviews	The Chemical Society (London)		1	1960
UMN	Uspekhi matematicheskikh nauk	Russian Mathematical Surveys	London Mathematical Society	15	1	1960
Usp. fiz. nauk	(see UFN)					
Usp. khim(ii)	(see UKh)					
Usp. matem. nauk	(see UMN)					
Usp. sovr. biol.	Uspekhi sovremennoi biologii	Russian Review of Biology	Oliver and Boyd		48	1959
Vest. mashinostroeniya	Vestnik mashinostroeniya	Russian Engineering Journal	Production Engineering Research Assoc.		4	1959
Vop. gem. i per. krovi	Voprosy gematologii i perelivaniya krovi	Problems of Hematology and Blood Transfusion	National Institutes of Health*		1	1957
Vop. onk.	Voprosy onkologii	Problems of Oncology	National Institutes of Health*		1	1957
Vop. virusol.	Voprosy virusologii	Problems of Virology	National Institutes of Health*		1	1957
Zav(odsk). lab(oratoriya)	Zavodskaya laboratoriya	Industrial Laboratory	Instrument Society of America	25	1	1959
ZhAKh Zh. anal(it). khimii	Zhurnal analiticheskoi khimii	Journal of Analytical Chemistry USSR	Consultants Bureau	7	1	1952
ZhETF Zh. éksperim. i teor. fiz.	Zhurnal éksperimental'noi i theoreticheskoi fiziki	Soviet Physics–JETP	American Institute of Physics	28	1	1955
ZhFKh Zh. fiz. khimii	Zhurnal fizicheskoi khimii	Russian Journal of Physical Chemistry	The Chemical Society (London)		7	1959
ZhMÉI Zh(urn). mikrobiol. épidemiol. i immunobiol.	Zhurnal mikrobiologii, épidemiologii i immunobiologii	Journal of Microbiology, Epidemiology and Immunobiology	National Institutes of Health*		1	1957
ZhNKh Zh(urn). neorgan(ich). khim(ii)	Zhurnal neorganicheskoi khimii	The Russian Journal of Inorganic Chemistry	The Chemical Society (London)		1	1959
ZhOKh Zh(urn). obshch(ei) khimii	Zhurnal obshchei khimii	Journal of General Chemistry USSR	Consultants Bureau	19	1	1949
ZhPKh Zh(urn). prikl. khimii	Zhurnal prikladnoi khimli	Journal of Applied Chemistry USSR	Consultants Bureau	23	1	1950
ZhSKh Zh(urn). strukt. khimii	Zhurnal strukturnoi khimii	Journal of Structural Chemistry	Consultants Bureau	1	1	1960
ZhTF Zh(urn). tekhn. fiz.	Zhurnal teknicheskoi fiziki	Soviet Physics–Technical Physics	American Institute of Physics	26	1	1956
Zh(urn). vyssh. nervn. deyat. (im. Pavlova)	Zhurnal vysshei nervnoi deyatel'nosti (im. I. P. Pavlova)	Pavlov Journal of Higher Nervous Activity	National Institutes of Health*		1	1958

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